Investigation of the origin and synthetic application of the pseudodilution effect for Pd-catalyzed macrocyclisations in concentrated solutions with immobilized catalysts

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abs.	absolute
alk.	alkyl
eq.	equivalents
ar.	aryl
calcd.	calculated
br s	broad singulett
ca.	circa
CH c	yclohexane
δ	chemical shitt (in relation to TMS)
d	dublett
TLC	thin layer chromatography
DCM	dichlormethane
dd	dublett of dublett
ddd	dublett of dublett
dt	dublett of triplett
DIAD	diisopropylazodicarboxylate
DIBAL	diisobutylaluminiumhydride
DIC	diisopropylcarbodiimide
DMAP	N,N-dimethylaminopyridine
DME	dimethoxyethane
DMF	N,N-dimethylformamide
DMSO	dimethylsulfoxide
EA	ethylacetate
EDC	3,3-dimethylaminopropyl-ethyl-carbodiimide hydrochloride
Et	ethyl
EtOH	ethanol
FAB	fast atom bombardment
GC-MS	gas chromatography – mass spectrometry coupling

HOBT	1-hydroxybenzotriazole
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
J	coupling constant
conz.	concentrated
m	multiplett
Me	methyl
MeOH	methanol
mmol	millimol
mol%	mol percent
mp	melting point
MS	mass spectrim
m/z	mass/charge
MW	microwave
3-NBA	3-nitrobenzylalcohol
NMM	N-methyl-morpholine
NMR	nuclear magnetic resonance
olefin.	olefinic
org.	organic
ppm	parts per million
PPTS	pyridinium-p-toluenesulfonate
prep.	preparative
PS	polystyrene
q	quadruplett
quant.	quantitative
R, R'	residue
RT	room temperature
8	singulett
std.	saturated
t	triplett
TBDMSCl	tert-butyldimethylsilyl-chloride
THF	tetrahydrofurane
TMS	tetramethylsilane resp. trimethylsilyl-
t _R	retention time

Equipment and reagents

NMR-spectroscopy

NMR-spectra were recorded on the following instruments:

Bruker AM 400 :	400 MHz ¹ H-NMR, 100.6 MHz ¹³ C-NMR
Varian Mercury 400 :	400 MHz ¹ H-NMR, 100.6 MHz ¹³ C-NMR

Chemical shifts are stated in ppm (referring to tetramethylsilane (TMS, $\delta = 0$ ppm) as internal standard. The coupling constants *J* are stated in Hertz (Hz). Signal multiplicities are abbreviated as following: s = singulett, d = doublett, dd = doublett of doubletts, t = triplett, dt = doublett of triplett, q = quartett, quint. = quintett, m = multiplett, br = broad signal.

High resolution mass spectrometry (HRMS)

The FAB-mass spectra were recorded on a Jeol SX 102A spektrometer. 3-Nitrobenzylalcohol (3-NBA) served as matrix. The stated values are m/z.

Melting points

Melting points have been measured on a Büchi Schmelzpunktmessgerät 530 and are uncorrected.

Chromatography

For analytical TLC SiO_2 -plates from Merck (Silica 60 F254) were used. For detection were used UVlight (wavelength 254 nm) and the following stains:

Reagent A: 12 g molybdatophosphoric acid in 250 ml ethanol

Reagenz B: 2.5 g molybdatophosphoric acid, 1 g cerium(IV)-sulfate, 6 ml conc. sulfuric acid and 94 ml H_2O

The corresponding eluents and Rf-values are stated in the characterization data of the compounds.

Purifications via flash chromatography were performed on silica (particle size: 40-60 μ m) from Baker with a pressure of 1.3-1.8 bar.

HPLC-chromatography

Preparative HPLC was performed with a Agilent (1100 Series) system. CC125/21 Nucleosil 120-5 C4, resp. CC125/21 Nucleodur 120-5 C18 Gravity columns from Macherey&Nagel were used. The flow

rates were 27 ml/min. Analytical HPLC was performed on a HP 1100–model from Hewlett-Packard with CC125/4 Nucleosil 120-5 C4 resp. CC125/4 Nucleodur 120-5 C18 Gravity column from Macherey&Nagel with flow rates of 1 ml/min. Detection occurred at wave lengths of 210 nm resp.254 nm. As eluents $H_2O+0.1$ Vol.-% TFA (A) and acetonitrile+0.1 Vol.-% TFA (B) were used.

Two standard gradients were used:

Gradient for C18 column (C18): 0.5 min 10 % B, then within 11 min to 100 % B.

Gradient for C4 column (C4): 1 min 10 % B, then within 11.7 min to 100 % B.

Gas-Chromatography

GC-MS-measurements were performed on a GC 6890 coupled to MS-detector 5973 from Hewlett-Packard with capillary column HP-5TA ($0.33 \mu m$, $25m \times 0.2 mm$ ID).

GC-MS(DB_100): 1 min at 100°C and then within 5 min to 300°C.

GC-MS(RP70): 2 min at 70°C and then within 6.5 min to 300°C.

Alle reagents were purchased from Acros Chimica, AdvancedChemtech, Aldrich, Fluka, Novabiochem, Riedel de Haen and Sigma. The used solvents were if necessary bought absolutely dry or dried according to the following procedures.

Dichlormethane	Refluxing and distillation first over P_2O_5 and then CaH_2
Diethylether	Refluxing and distillation over sodium
Methanol	Refluxing and distillation over magnesium
Triethylamine	Refluxing and distillation over CaH ₂
Tetrahydrofurane	Refluxing and distillation over sodium/potassium
Toluene	Refluxing and distillation over sodium

Experiments related to preparation of Pd-catalyst beads

General procedure for the synthesis of solid phase bound ligand 1a-g/Pd (GP1)

In a Schlenk tube under inert conditions aminomethyl-beads are swollen in abs. toluene. The solvent is condensed off under oil pump vacuum to remove the oxygen within the beads. A second inert Schlenk

tube is charged with paraformaldehyde (4 eq in respect to the bead-loading), abs. methanol (10 ml per 1 g paraformaldehyde) and diphenylphosphine (4 eq in respect to the bead-loading). The reaction mixture is heated at 60 °C until a clear solution forms (after ca. 48 h). The solvent is removed in oil pump vacuum using a cooling trap. The oily residue is dissolved in abs. toluene (1.5 ml per 1 g paraformaldehyde). This solution is added to the first Schlenk with the beads, which have been swollen in abs. toluene (10 ml per 1 g beads). The suspension is heated for 2 d at 105°C upon which water drops are condensing in the cold upper part of the Schlenk tube. After cooling to RT the beads are collected by filtration under argon, washed with 4x abs. toluene, 2x abs. DCM/THF (1/1) mixture and 3x abs. DCM. The beads are dried overnight in oil pump vacuum.

Resin	Producer Article Number	Mesh	DVB in%	Loading of original resin (NH ₂) in mmol\g	Calculated loading of modified resin (PPh ₂) in mmol\g
1a	Novabiochem 01-64-0010	200-400	1	1.13	0.77
1b	Novabiochem 01-64-0143	100-200	1	0.78	0.59
1c	Novabiochem 01-64-0198	70-90	1	1.17	0.79
1d	Fluka 17301	70-100	1	1.0	0.72
1e	Advanced Chem Tech	ca 120	1	0.33	0.29
1f	Rapp Polymere H 50056002	ca 20	1	0.95	0.68
1g	Argonaut 495638 (Aldrich)	ca 100	"high"	1.39	0.90

Calculation of the theoretical resin loading (PPh_2) in mmol/g after the reaction:

 $\begin{aligned} & \text{Original Resin Loading [mmol NH_2/g] * 1 g} \\ & \text{Theoretical Resin Loading [mmol ((CH_2)PPh_2)_2/g] = } \\ & 1 \text{ g + Original Resin Loading [mmol NH_2/g] * 0.001 * (M_{(CH_2)PPh_2)_2} - M_{H_2})} \end{aligned}$

Determination of actual loading **1a**(PPh₂) by elemental analysis

•*Theoretical Value* for elemental analyis of %P and %N:

Theoretical loading of $1a(PPh_2) \ge M_p \ge 0.77 \ge 31 \ge 247.7 \text{ mg/g} = 4.77\%P$

Theoretical loading of $1a(PPh_2) \ge M_N = 0.77 \ge 14 = 1.08\% N$

•*Experimental Value* (Elemental analysis by Mikroanalytisches Laboratorium H. Kolbe, Mülheim/Ruhr) %P = 4.69%

% N = 1.05%

Experimental Value = $%P/(31 \times 2) = 0.76 \text{ mmol/g}$

Control: % N / 14 = 0.75 mmol/g

As the resin modification has been shown to work quantitative, the calculated values were taken for all other resins.

General procedure for the synthesis of solid phase bound Pd-catalyst 1a/Pd-1g/Pd (GP2)

In a dry Schlenk tube the modified ligand beads **1a-g** are inertized by 3 vacuum/argon cycles and then swollen in abs. toluene for 5 min. $Pd[PPh_3]_4$ (1.1 eq in respect to ligand loading) is added. The Schlenk flask is shaken for 30 min and the yellow suspension heated for 24 h to 60°C under light protection. After cooling to RT the beads are collected by filtration under argon, washed with 2x abs. diethylether (slighly yellow wash solutions), 1x abs. ethanol (slighly yellow wash solutions), 5x abs. THF (the first 3 wash solutions are slightly yellow, the last 2 colorless) and 2x abs. diethylether (colorless wash solutions) and dried overnight in oil pump vacuum.

Catalyst name	Theoretical resin $((CH_2)PPh_2)_2)$ in mmol/g	loading
1a/Pd	0.52	
1b/Pd	0.43	
1c/Pd	0.53	
1d/Pd	0.49	
1e/Pd	0.24	
1f/d	0.48	
1g/Pd	0.57	

Calculation of the theoretical loading in mmol/g after reaction:

Theoretical Catalyst Loading [mmol Pd/g] =	Theoretical Resin Loading [mmol ((CH ₂)PPh ₂) ₂ /g] * 1 g
	1 g + Theoretical Resin Loading [mmol ((CH ₂)PPh ₂) ₂ /g] * 0.001 * $M_{Pd(PPh3)2}$

Experiments related to Tsuji-Trost-allylation

General procedure for Fischer-esterification (GP3)

The carboxylic acid is dissolved in MeOH and conc. H_2SO_4 is added. The solution is heated under reflux overnight. Then the volatiles are removed in vaccuo using a rotovap. The residue is dissolved in 200 ml ethylacetate, washed with 10% NaHCO₃-solution (3x70 ml) and brine (1x70 ml). The organic phase is dried over Na₂SO₄. After concentration in vaccuo the crude product is purified via flash chromatography.

General procedure for the mono-silylation of a diol (GP4)

To a suspension of 1 eq sodium hydride in abs. THF is added 1 eq diol. After stirring at RT for 2 h 1 eq *tert*-butyldimethylsilylchloride are added and the reaction mixture stirred at RT overnight. The

reaction mixture is diluted with diethylether (100 ml) and washed with 10% NaHCO₃ solution (30 ml) and brine (30 ml) and dried over Na_2SO_4 . After concentration in vaccuo the crude product is purified via flash chromatography.

General procedure for the mono-silylation of a glycol (GP5)

Under an inert atmosphere to a solution of 6 eq glycol in DCM are added 1 eq abs. triethylamine, 0.5 eq. DMAP and 1 eq *tert*-butyldimethylsilylchloride. The reaction mixture is stirred for 2 h at RT, then diluted with 100 ml diethylether. The organic phase is washed with 10% NaHCO₃ (30 ml) and brine (30 ml) and dried over Na₂SO₄. After concentration in vaccuo the crude product is purified via flash chromatography.

General procedure for Swern-oxidation (GP6)

In an inert atmosphere a flask is charged with 1.5 eq oxalylchloride in abs. DCM, to which 3 eq DMSO are slowly added at -78° , upon which gas evolution is observed. After 10 min a solution of 1 eq alcohol in DCM is slowly added and stirred for 1.5 h. Then 5 eq abs. triethylamine are added to the reaction mixture. The reaction mixture is let to warm up overnight. After dilution with 200 ml diethylether, the organic phase is washed with 5% HCl (3x70 ml), 10% NaHCO₃-solution (2x70 ml) and H₂O (70 ml), and then dried over Na₂SO₄. After concentration in vaccuo the crude product is used without further purification.

General procedure for the formation of a vinylepoxide (GP7)

In a Schlenk flask 1.5 eq allylic bromide are dissolved in MeOH and H_2O . 3.0 eq tetrahydrothiophene are added and the mixture stirred for 1 h. With the help of a cooling trap the volatiles are removed in vaccuo. The gel-like residue is then dissolved in DCM. In a 250-ml flask a solution of 1 eq aldehyde in DCM is prepared, a spatula tip of benzyl-trimethylammoniumchloride is added and the solution is cooled to -20°C in a MeOH/ice-bath. To this aldehyde solution is added the previously prepared solution of the sulfonium salt followed by precooled 10 M NaOH, which is added in one portion. The reaction mixture is heavily stirred and in the thawing cooling bath brought to RT overnight.

The reaction mixture is diluted with 100 ml diethylether and washed with H_2O (70 ml). The aqueous layer is extracted with diethylether (4x30 ml). The combined organic layers are dried over Na_2SO_4 . After concentration in vaccuo the crude product is purified via flash chromatography.

General procedure for the deprotection of TBDMS-group (GP8)

To a solution of 1 eq TBDMS-protected alcohol in MeOH are added 11.5 eq ammoniumfluoride. The reaction mixture is heated under reflux for 2.5 h. The solvent is removed in vaccuo using a rotovap. The residue is taken up in H_2O (100 ml) and extracted with ethylacetate (4x 30 ml). The combined

organic layers are dried over Na_2SO_4 . After concentration in vaccuo the crude product is purified via flash chromatography.

General procedure for carbodiimide-mediated esterification (GP9)

To a solution of 1.1 eq acid, 0.5 Äq DMAP and 1.0 eq alcohol in DCM are added 0°C 1.1 eq DIC or EDC. After stirring the reaction mixture overnight, the organic phase is washed with H₂O (3x10 ml), 10% NaHCO₃-solution (3x10 ml) and brine (3x10 ml). The combined organic layers are dried over Na₂SO₄. After concentration in vaccuo the crude product is purified via flash chromatography.

General procedure for Tsuji-Trost-cyclisation (GP10)

In an inert 5 ml-flask 0.1 eq Pd-catalyst beads are inertized by 3 vacuum/argon cycles. After addition of THF the reaction mixture is heated to 75°C under argon. After 30 min 1 eq substrate are added and the reaction mixture heated for another 15 h. After cooling to RT the beads are filtered, and washed with DCM (1x45 ml, 10 min), DCM/MeOH (1/1) (2x20 ml, 2x10min) and DCM (1x20 ml, 10 min). The combined organic extracts are concentrated in vaccuo and the crude product is purified via prep. HPLC (EGC18).

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6-Bromohexanoic acid methylester (41)

The synthesis proceeded according to **GP3** with 5.00 g (25.63 mmol) 6-bromohexanoic acid (6), 40 ml methanol and 1 ml conc. sulfuric acid. The crude product was purified via flash chromatography (silica, column \emptyset = 5 cm, length: 20 cm, cyclohexane:ethylacetate 10:1).

 $R_{\rm f} = 0.33$

Yield : 3.61 g (17.3 mmol, 66 %) colorless oil

¹H-NMR (400 MHz, CDCl₃): $\delta = 3.59$ (s, 3H, -OCH₃), 3.35 (t, J = 6.8 Hz, Br-CH₂-R), 2.27 (t, J = 7.3 Hz, 2H, R-CH₂-COOMe), 1.81 (quin, J = 7.2 Hz, 2H, Br-CH₂-CH₂-R), 1.60 (quin, J = 7.5 Hz, 2H, R-CH₂-CH₂-COOMe), 1.42 (quin, J = 7.7 Hz, 2H, Br-CH₂-CH₂-CH₂-R)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.8$ (C=O), 51.8 (-OCH₃), 34.1 (R-<u>C</u>H₂-CH₂-COOMe), 33.7 (Br-<u>C</u>H₂-R), 32.7 (R-<u>C</u>H₂-CH₂-CH₂-COOMe), 28.0 (Br-CH₂-<u>C</u>H₂-R), 24.4 (R-<u>C</u>H₂-COOMe)

The analytical data are in accordance to the literature.ⁱ

7,7-Bis-(phenylsulfonyl)-heptanoic acid methylester (42)

Three Schlenk-flask were dried in vacuum and filled with argon. In the first Schlenk-flask a solution of 3.61 g (17.3 mmol, 1.0 eq.) 6-bromohexanoic acid methylester (**41**) in 10 ml abs. *N*,*N*-dimethylformamide was prepared, in the second Schlenk-flask a solution of 5.13 g (PhSO₂)₂CH₂ (17.3 mmol, 1.0 eq.) in 20 ml abs. *N*,*N*-dimethylformamide. In the third Schlenk-flask a suspension of 414 mg NaH (17.3 mmol, 1.0 eq.) in 10 ml abs. DMF was prepared, cooled in an ice bath, and then the solution of bis(phenylsulfonyl) methane was slowly dropped to the NaH-suspension, upon which gas evolution was observed. After 90 min the formed yellow solution was added to the 6-bromohexanoic acid solution in the first Schlenk flask drop by drop. The reaction mixture was stirred at 60°C overnight. The reaction mixture was treated with 250 ml ethylacetate and 70 ml 5% HCl. The organic layer was washed with H₂O (70 ml) and brine (70 ml). The combined organic layers were dried over Na₂SO₄. After concentration in vaccuo the crude product was purified via flash chromatography (silica, column \emptyset = 5 cm, length: 23 cm, cyclohexane:ethylacetate 3:2).

 $R_{\rm f} = 0.51$

Yield : 6.33 g (14.9 mmol, 92 %) colorless solid

¹H-NMR (400 MHz, CDCl₃) : δ = 7.96-7.93 (m, 4H, ar. H), 7.71-7.67 (m, 2H, ar. H), 7.60-7.54 (m, 4H, ar. H), 4.38 (t, *J* = 5.6 Hz, 1H, R-C<u>H</u>-(SO₂Ph)₂), 3.6 (s, -OCH₃), 2.25 (t, *J* = 7.4 Hz, 2H, R-C<u>H</u>₂-COOMe), 2.17-2.12 (m, 2H, (PhSO₂)₂CH-C<u>H</u>₂-R), 1.62-1.51 (m, 4H, alk. H), 1.30-1.23 (m, 2H, alk. H)

¹³C-NMR (100 MHz, CDCl₃) : $\delta = 173.9$ (C=O) 138.0 (ar. C), 134.7 (ar. C), 129.8 (ar. C), 129.6 (ar. C), 129.3 (ar. C), 129.1 (ar. C), 83.9 (PhSO₂-<u>C</u>HR-SO₂Ph), 51.9 (-OCH₃), 28.8 ((PhSO₂)₂CH-CH₂-CH₂-CH₂-R), 28.1 ((PhSO₂)₂CH-CH₂-CH₂-CH₂-R), 27.3 ((PhSO₂)₂CH-CH₂-<u>C</u>H₂-R), 25.9 ((PhSO₂)₂-CH-<u>C</u>H₂-R), 24.6 (R-<u>C</u>H₂-COOMe)

HRMS (FAB, 3-NBA) for $C_{20}H_{25}O_6S_2 [M+H]^+$: calcd.: 425.1093 found: 425.1096

7,7-Bis-(phenylsulfonyl)-heptanoic acid (7)

6.33 g (14.9 mmol, 1.0 eq.) 7,7-bis-(phenylsulfonyl)-heptanoic acid methylester (**42**) were dissolved in 20 ml methanol. Then 20 ml tetrahydrofurane, 7 ml H₂O and 1.87 g (44.56 mmol, 3.0 eq.) LiOH H₂O were added. The reaction mixture was stirred at 40°C for 18 h. Then the solvents were removed in vaccuo using a rotovap. The residue was taken up in 100 ml ethylacetate and 40 ml H₂O. After phase separation the organic layer was discarded. The aqueous layer was acidified to pH 1 and extracted with ethylacetate (3x150 ml). The combined organic layers were dried over Na₂SO₄. After concentration in vaccuo the crude product was purified via flash chromatography (silica, column \emptyset = 5 cm, length: 23 cm, ethylacetate:methanol 40:1).

 $R_{\rm f}\,{=}\,0.58$

Yield: 6.65 g (12.86 mmol, 86 %) colorless crystals

mp: 81.0°C

¹H-NMR (400 MHz, MeOD): $\delta = 7.93-7.90$ (m, 4H , ar. H), 7.76-7.71 (m, 2H, ar. H), 7.62-7.58 (m, 4H, ar. H), 5.05 (t, J = 5.5 Hz, 1H, C<u>H</u>-(SO₂Ph)₂), 4.86 (br s, COOH), 2.21 (t, J = 7.3 Hz, 2H, C<u>H</u>₂-COOMe), 2.16-2.11 (m, 2H, (PhSO₂)₂CH-C<u>H</u>₂), 1.54-1.44 (m, 4H, alk. H), 1.24 (t, J = 7.2 Hz, 2H, alk. H)

¹³C-NMR (100 MHz, CDCl₃) : δ = 171.3 (C=O) 138.0 (ar. C), 134.7 (ar. C), 129.8 (ar. C), 129.3 (arom C), 83.9 (PhSO₂-<u>C</u>HR-SO₂Ph), 28.8 ((PhSO₂)₂CH-CH₂-CH₂-CH₂-R), 28.1 ((PhSO₂)₂CH-CH₂-CH₂-CH₂-CH₂-R), 25.9 ((PhSO₂)₂-CH-<u>C</u>H₂-R), 24.5 (R-<u>C</u>H₂-COOMe)

HRMS (FAB, 3-NBA) for $C_{19}H_{23}O_6S_2$ [M+H]⁺: calcd.: 411.0936

found.: 411.0920

6-(tert-Butyl-dimethyl-silanyloxy)-hexan-1-ol (51)

The synthesis proceeded according to **GP4** with 4.46 g (186 mmol) NaH in 140 ml abs. THF, 22.0 g (186 mmol) 1,6-hexandiol (2) and 28.0 g (186 mmol) *tert*-butyldimethylsilylchloride. The crude product was purified via flash chromatography (silica, column \emptyset = 7 cm, length: 23 cm, pentane:ethylacetate 7:1).

 $R_{\rm f} = 0.39$

Yield: 16.3 g (70.2 mmol, 38 %) colorless oil.

¹H-NMR (400 MHz, CDCl₃): δ = 3.68-3.60 (br m, 4 H, CH₂OSi und C<u>H</u>₂OH), 1.63 (br s, 1H, -OH), 1.60-1.53 (br m, 4 H, alk. CH₂), 1.39-1.35 (br m, 4 H, alk. CH₂), 0.90 (s, 9H, *tert*-Butyl), 0.06 (s, 6H, (CH₃)₂Si).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 63.18$ (CH₂OSi), 62.93 (CH₂OH), 32.86 (alk. CH₂), 26.07 (alk. CH₂), 25.71 (alk. CH₂), 25.64 (C(<u>C</u>H₃)₃), 18.49 (<u>C</u>(CH₃)₃), -5.09 (Si(CH₃)₂)

The analytical data are according to literature.ⁱⁱ

10-(tert-Butyl-dimethyl-silanyloxy)-decan-1-ol (57)

The synthesis proceeded according to **GP4** with 0.64 g (27.0 mmol) NaH in 40 ml abs. THF, 4.7 g (27.0 mmol) 1,10-decandiol and 4.10 g (27.0 mmol) *tert*-butyldimethylsilylchloride. The crude product was purified via flash chromatography (silica, column \emptyset = 5 cm, length: 20 cm, pentane:ethylacetate 7:1).

 $R_{\rm f}\,{=}\,0.51$

Yield: 2.09 g (7.3 mmol, 27 %) colorless oil

¹H-NMR (400 MHz, CDCl₃): δ = 3.65-3.57 (br m, 4 H, CH₂OSi und C<u>H</u>₂OH), 1.63 (br s, 1H, -OH), 1.60-1.45 (br m, 4H, alk. CH₂), 1.39-1.20 (br m, 12H, alk. CH₂), 0.89 (s, 9H, *tert*-Butyl), 0.05 (s, 6H, (CH₃)₂Si).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 63.34$ (CH₂OSi), 60.41 (CH₂OH), 32.95 (alk. CH₂), 29.64 (alk.CH₂), 29.51 (alk. CH₂), 26.08 (alk. CH₂), 25.89 (C(<u>C</u>H₃)₃), 18.49 (<u>C</u>(CH₃)₃), -5.08 (Si(CH₃)₂)

The analytical data are according to literature.ⁱⁱ

6-(tert-Butyl-dimethyl-silanyloxy)-hexanal (3)

The synthesis proceeded according to **GP6** with 2.8 ml (26.1 mmol) oxalylchloride in 60 ml DCM, 3.7 ml (52.2 mmol) DMSO, a solution of alcohol **51** in 20 ml DCM and 12.1 ml (87.0 mmol) abs. triethylamine.

Yield: 4.04 g (17.4 mmol, 99 %) orange oil.

¹H-NMR (400 MHz, CDCl₃): δ = 9.73 (s, 1H, CHO), 3.58 (t, *J* = 6.5 Hz, 2 H, CH₂OSi), 2.41 (td, *J* = 7.4 Hz, 1.8 Hz, 2H, CH₂CHO), 1.62 (quin, *J* = 7.5 Hz, 2H, alk. CH₂), 1.54-1.49 (m, 2H, alk. CH₂), 1.41-1.35 (m, 2H, alk. CH₂), 0.88 (s, 9H, *tert*-Butyl), 0.03 (s, 6H, (CH₃)₂Si).

HRMS (FAB, 3-NBA) for $C_{12}H_{25}O_2Si [M-H]^+$:	calcd:	229.1624
	found:	229.1609

The analytical data are according to literature.ⁱⁱⁱ

10-(tert-Butyl-dimethyl-silanyloxy)-decanal (58)

The synthesis proceeded according to **GP6** with 1.2 ml (10.9 mmol) oxalylchloride in 30 ml DCM, 1.5 ml (21.8 mmol) DMSO, a solution of 2.09 g (7.26 mmol) 10-(*tert*-butyl-dimethyl-silanyloxy)-decan-1- ol (**57**) in 20 ml DCM and 5.1 ml (36.3 mmol) abs. triethylamine.

Yield: 2.13 g (7.26 mmol, 99 %) orange oil.

¹H-NMR (400 MHz, CDCl₃): δ = 9.73 (s, 1H, CHO), 3.58 (t, *J* = 6.5 Hz, 2 H, CH₂OSi), 2.41 (td, *J* = 7.4 Hz, 1.8 Hz, 2H, CH₂CHO), 1.60-1.45 (br m, 4H, alk. CH₂), 1.39-1.20 (br m, 12H, alk. CH₂), 0.88 (s, 9H, *tert*-Butyl), 0.05 (s, 6H, (CH₃)₂Si).

The analytical data are according to literature.^{iv}

tert-Butyl-dimethyl-[5-(3-vinyl-oxiranyl)-pentyloxy]-silane (52)

The synthesis proceeded according to **GP7** with 2.3 ml (26.3 mmol) allylic bromide dissolved in 7.8 ml methanol and 0.85 ml H₂O, 4.7 ml (52.6 mmol) tetrahydrothiophene. The gel-like residue was taken up in 13.5 ml DCM and added to a solution of 4.04 g (17.4 mmol) 6-(tert-butyl-dimethyl-silanyloxy)-hexanal (**3**) in 20 ml DCM, immediately followed by 33.5 ml precooled 10 M NaOH.

The crude product was purified via flash chromatography (silica, column \emptyset = 5 cm, length: 20 cm, cyclohexane:ethylacetate 20:1).

 $R_{\rm f} = 0.32$

Ausbeute : 3.38 g (12.7 mmol, 73%) yellowish oil

¹H-NMR (400 MHz, CDCl₃) : $\delta = 5.70-5.52$ (m, 1H, R-C<u>H</u>=CH₂, 2 diastereomers), 5.48-5.40 (m, 1H, R-CH=C<u>H</u>₂ cis, 2 diastereomers), 5.35-5.22 (m, 1H, R-CH=C<u>H</u>₂ trans, 2 diastereomers), 3.59 (t, J = 6.5 Hz, 2H, R-C<u>H</u>₂-COOR⁴), 3.08 (dd, J = 2.1 Hz, 7.4 Hz, 1H, (R-CH₂)C<u>H</u>(O_{epoxid})CH-CH=CH₂), 2.81 (dt, J = 2.1 Hz, 5.6 Hz, 1H, CHO_{epox}), 1.60-1.36 (m, 8H, alk. H), 0.88 (s, 9H, *tert*-Butyl), 0.04 (s, 6H, (CH₃)₂Si)

HRMS (FAB, 3-NBA) for $C_{12}H_{25}O_2Si [M-H]^+$: calcd.: 269.1936

found.: 269.1920

tert-Butyl-dimethyl-[9-(3-vinyl-oxiranyl)-nonyloxy]-silane (59)

The synthesis proceeded according to **GP7** with 0.94 ml (10.9 mmol) allylic bromide dissolved in 3.2 ml methanol and 0.35 ml H₂O, and 1.9 ml (21.8 mmol) tetrahydrothiophene. The gel-like residue was taken up in 7.9 ml dichlormethane and added to a solution of 2.13 g (7.3 mmol) 10-(*tert*-butyl-dimethyl-silanyloxy)-decanal (**58**) in 6 ml DCM, immediately followed by 13.9 ml precooled 10 M NaOH.

The crude product was purified via flash chromatography (silica, column \emptyset = 4 cm, Länge: 20 cm, cyclohexane:ethylacetate 50:1).

 $R_{\rm f}\,{=}\,0.28$

Yield: 1.58 g (4.8 mmol, 67%) yellowish oil

¹H-NMR (400 MHz, CDCl₃) : $\delta = 5.76-5.33$ (m, 1H, -C<u>H</u>=CH₂,), 5.38-5.456 (ddd, J = 1.6 Hz, 8.7 Hz, 17.2 Hz, 1H, -CH=C<u>H</u>₂), 5.30 (dd, J = 0.73 Hz, 10.2 Hz, 1H, -CH=C<u>H</u>₂), 3.60 (t, J = 6.6 Hz, 2H, R-C<u>H</u>₂-COOR⁴), 3.09 (dd, J = 2.1 Hz, 7.3 Hz, 1H, (R-CH₂)C<u>H</u>(O_{Epoxid})CH-CH=CH₂), 2.82 (td, J = 5.6 Hz, 2.2 Hz, 1H, CHO_{epox}), 1.60-1.55 (m, 2H, -C<u>H</u>₂-epoxide),1.52-1.38 (m, 4H, alk.H), 1.30-1.25 (m, 10H, alk.H), 0.90 (s, 9H, *tert*-Butyl), 0.05 (s, 6H, (CH₃)₂Si)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 135.8$ (-<u>C</u>H=CH₂), 118.7 (-CH=<u>C</u>H₂), 63.34 (-CH₂OSi-), 60.52 (CH₂-O), 58.78 (CH₂-O), 32.97 (alk. C), 32.08 (alk. C), 29.53 (alk. C), 27.86 (alk. C), 26.10 ((<u>C</u>H₃)₃C), 18.52 (<u>C</u>(CH₃)₃), -5.05 (CH₃-Si).

5-(3-Vinyl-oxiranyl)-pentan-1-ol (5)

The synthesis proceeded according to **GP8** with 1.94 g (7.3 mmol) *tert*-butyl-dimethyl-[5-(3-vinyl-oxiranyl)-pentyloxy]-silane (**52**) in 150 ml methanol and 3.1 g (83.5 mmol) ammoniumfluoride. The

crude product was purified via flash chromatography (silica, column \emptyset = 5 cm, length: 20 cm, cyclohexane:ethylacetate 1:1).

 $R_{\rm f}\,{=}\,0.32$

Yield: 0.72 g (4.6 mmol, 63%) yellowish oil

¹H-NMR (400 MHz, CDCl₃) : δ = 5.56-5.18 (m, 3H, olefin. H), 3.57 (t, *J* = 6.5 Hz, 2H, C<u>H</u>₂OH), 3.05 (dd, *J* = 7.4 Hz, 2.2 Hz, 1H, CHO_{epox}), 2.78 (td, *J* = 5.5 Hz, 2.0 Hz, 1H, CHO_{epox}), 1.58-1.34 (m, 8H, alk. H).

HRMS (FAB, 3-NBA) for $C_9H_{16}O_2Na [M+Na]^+$:	calcd.:	179.1048
	found:	179.1034

9-(3-Vinyl-oxiranyl)-nonan-1-ol (60)

The synthesis proceeded according to **GP8** with 1.57 g (4.8 mmol) *tert*-butyl-dimethyl-[6-(3-vinyl-oxiranyl)-nonyloxy]-silane (**59**) in 185 ml methanol and 3.2 g (85.4 mmol) ammoniumfluoride. The crude product was used without further purfication.

 $R_{\rm f} = 0.54$ (cyclohexane:ethylacetate 1:1)

Yield: 0.98 g (4.6 mmol, 96%) yellowish oil

¹H-NMR (400 MHz, CDCl₃) : δ = 5.56-5.18 (m, 3H, olefin. H), 3.57 (t, *J* = 6.5 Hz, 2H, C<u>H</u>₂OH), 3.05 (dd, *J* = 7.4 Hz, 2.2 Hz, 1H, CHO_{epox}), 2.78 (td, *J* = 5.5 Hz, 2.0 Hz, , 1H, CHO_{epox}), 1.58-1.34 (m, 8H, alk. H).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 135.7$ (-<u>C</u>H=CH₂), 118.7 (-CH=<u>C</u>H₂), 63.01 (-CH₂OSi-), 60.520 (CH₂-O), 58.77 (CH₂-O), 32.84 (alk. C), 32.03 (alk. C), 29.50 (alk. C), 27.81 (alk. C), 26.34 (alk.C), 25.81 (alk.C).

Tri(ethylenglycol)-mono-tert-butyldimethylsilyl ether (61)

The synthesis proceeded according to **GP5** with 19.0 ml (142.3 mmol) triethylenglycol, 3.81 g (25.3 mmol) *tert*-butyldimethylsilylchloride, 0.65 g (6.4 mmol) DMAP and 3.5 ml (25.0 mmol) abs. triethylamine in 50 ml abs. DCM. The crude product was purified via flash chromatography (silica, column \emptyset = 5 cm, length: 20 cm, eluent: ethylacetate).

 $R_{\rm f}\,{=}\,0.64$

Yield: 4.81 g (18.2 mmol, 64%) yellowish oil

GC-MS(DB_100): $t_R = 3.86 \text{ min } [M]^+ = 265$

¹H-NMR (400 MHz, CDCl₃) : $\delta = 3.76$ (t, J = 5.38 Hz, 2H, Si-O-CH₂-CH₂-O), 3.72–3.70 (m, 2H, O-CH₂), 3.66 (s, 4H, O-CH₂), 3.61–3.59 (m, 2H, O-CH₂), 3.56 (t, 2H, J = 5.38 Hz, Si-O-CH₂-CH₂), 0.88 (s, 9H, Si-C-(CH₃)₃), 0.06 (s, 6H, Si-(CH₃)₂).

¹³C-NMR (100 MHz, CDCl₃): δ = 72.7 (HO-CH₂-), 72.4 (CH₂-O), 70.8 (CH₂-O), 70.5 (CH₂-O), 62.7 (CH₂-O), 61.8 (CH₂-O), 26.0 ((<u>C</u>H₃)₃C), 18.5 (<u>C</u>(CH₃)₃), -5.13 (CH₃-Si).

The analytical data are according to literature.^v

Tetra(ethylenglycol)-mono-tert-butyldimethylsilylether (62)

The synthesis proceeded according to **GP5** with 24.3 g (125.0 mmol) tetraethylenglycol, 3.77 g (25.0 mmol) *tert*-butyldimethylsilylchloride, 0.61 g (5.0 mmol) DMAP and 3.5 ml (25.0 mmol) abs. triethylamine in 50 ml abs. DCM. The crude product was purified via flash chromatography (silica, column \emptyset = 5 cm, length: 20 cm, ethylacetate).

 $R_{\rm f} = 0.60$

Yield: 5.01 g (16.3 mmol, 65%) yellowish oil

GC-MS(DB_100): $t_R = 4.67 \text{ min } [M]^+ = 309$

¹H-NMR (400 MHz, CDCl₃): δ = 3.53-3.77 (m, 16H, alk. H), 0.88 (s, 9H, Si-C-(CH₃)₃), 0.05 (s, 6H, Si-(CH₃)₂).

¹³C-NMR (100 MHz, CDCl₃): δ = 73.6, 71.4, 71.3, 64.0, 62.7 (CH₂-O), 61.8 (CH₂-O), 26.1 ((<u>C</u>H₃)₃C), 18.5 (<u>C</u>(CH₃)₃), -5.13 (CH₃-Si).

The analytical data are according to literature.^{vi}

2-(2-tert-Butyldimethylsilyloxy-ethoxy)-ethoxy-acetaldehyde (63)

The synthesis proceeded according to **GP6** with 2.9 ml (27.3 mmol) oxalylchloride in 60 ml DCM, 3.9 ml (54.6 mmol) DMSO, a solution of 4.81 g (18.2 mmol) alcohol **61** in 20 ml DCM, and 12.7 ml (91.0 mmol) abs. triethylamine.

Yield: 4.1 g (15.6 mmol, 86%) orange-red oil

GC-MS(DB_100): $t_R = 3.69 \text{ min } [M]^+ = 263$

¹H-NMR (400 MHz, CDCl₃) : $\delta = 9.68$ (s, 1H, -CHO), 4.12 (s, 2H, CH₂-CHO), 3.73 (t, J = 5.28 Hz, 2H, CH₂-O), 3.71–3.67 (m, 4H, CH₂-O), 3.52 (t, J = 5.18 Hz, 2H, CH₂-O), 0.85 (s, 9H, Si-C(CH₃)₃), 0.03 (s, 6H, Si(CH₃)₂).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 200.5$ (-CHO), 72.7 (CH₂-O), 71.2 (CH₂-O), 70.8 (CH₂-O), 62.6 (CH₂-O), 25.9 (C(<u>C</u>H₃)₃), 18.4 (<u>C</u>(CH₃)₃), -5.19 (Si(CH₃)₂).

2-[2-(2-tert-Butyldimethylsilyloxy-ethoxy)-ethoxy]-ethoxy-acetaldehyde (64)

The synthesis proceeded according to **GP6** with 2.6 ml (24.0 mmol) oxalylchloride in 40 ml DCM, 3.4 ml (48.0 mmol) DMSO, a solution of 5.01 g (16.3 mmol) alcohol **2** in 20 ml DCM, and 11.2 ml (80.0 mmol) abs. triethylamine.

Yield: 4.45 g (14.8 mmol, 91%) yellowish oil

¹H-NMR (400 MHz, CDCl₃) : δ = 9.72 (s, 1H, -CHO), 4.14 (s, 2H, C<u>H</u>₂-CHO), 3.76-3.53 (m, 13H, CH₂-O), 0.90 (s, 9H, Si-C(CH₃)₃), 0.09 (s, 6H, Si(CH₃)₂).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 200.7$ (-CHO), 72.7 (CH₂-O), 71.2 (CH₂-O), 70.8 (CH₂-O), 62.6 (CH₂-O), 26.1 (C(<u>C</u>H₃)₃), 18.5 (<u>C</u>(CH₃)₃), -5.19 (Si(CH₃)₂).

tert-Butyl-dimethyl-{2-[2-(3-vinyl-oxiranylmethoxy)-ethoxy]-ethoxy}-silane (65)

The synthesis proceeded according to **GP7** with a solution of 1.98 ml (22.7 mmol) allylic bromide in 7.8 ml methanol and 0.85 ml H₂O, and 4.0 ml tetrahydrothiophene. The gel-like residue was taken up in 13.5 ml DCM and added to a solution of 3.99 g (15.1 mmol) aldehyd **64** in 20 ml DCM, immediately followed by 33.5 ml 10M NaOH. The crude product was purified via flash chromatography (silica, column \emptyset = 2 cm, length: 18 cm, cyclohexane:ethylacetate 3:1).

 $R_{\rm f}\,{=}\,0.44$

Yield: 2.45 g (8.1 mmol, 53%) yellow-orange oil

GC-MS(DB_100): $t_R = 4.42 \text{ min } [M]^+ = 303$

¹H-NMR (400 MHz, CDCl₃) : $\delta = 5.57$ (m, 1H, CH=C<u>H</u>₂), 5.42 (dd, J = 17.2 Hz, 2.0 Hz, 1H, C<u>H</u>=CH₂), 5.23 (dd, J = 9.8 Hz, 0.7 Hz, 1H, CH=C<u>H</u>₂), 3.72 (m, 4H, CH₂-O), 3.60 (m, 4H, CH₂-O), 3.48 (m, 4H, CH₂-O), 3.21 (dd, J = 7.0 Hz, 2.2 Hz, 1H, -C<u>H</u>O_{epox}-CH), 3.01 (ddt, J = 3.0 Hz, 3.4 Hz, 2.3 Hz, 1H, CH₂-C<u>H</u>O-CHO), 0.83 (s, 9H, C(CH₃)₃), 0.00 (s, 6H, Si(CH₃)₂).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 134.6$ (CH₂=<u>C</u>H-), 119.5 (CH₂=), 72.51 (CH₂-O), 70.67 (CH₂-O), 70.53 (CH₂-O), 62.57 (CH₂-O), 58.52 (CH-O), 55.89 (CH-O), 25.86 (C(<u>C</u>H₃)₃), 18.34 (<u>C</u>(CH₃)₃), -5.26 (Si(CH₃)₂).

tert-Butyl-dimethyl-(2-{2-[2-(3-vinyl-oxiranylmethoxy)-ethoxy]-ethoxy}-ethoxy)-silane (66)

The synthesis proceeded according to **GP7** with a solution of 1.88 ml (21.8 mmol) allylic bromide in 9.0 ml methanol and 1.0 ml H₂O, and 3.8 ml (43.5 mmol) tetrahydrothiophene. The gel-like residue was taken up in 13.5 ml DCM and added to a solution of 4.45 g (14.8 mmol) aldehyde **64** in 20 ml DCM, immediately followed by 33.5 ml 10M NaOH. The crude product was purified via flash chromatography (silica, column \emptyset = 2 cm, length: 18 cm, cyclohexane:ethylacetate 20:1).

 $R_{\rm f}\,{=}\,0.92$

Yield: 3.20 g (10.2 mmol, 69%) colorless oil

GC-MS(DB_100): $t_R = 5.15 \text{ min}$

¹H-NMR (400 MHz, CDCl₃) : $\delta = 5.57$ (m, 1H, CH=C<u>H</u>₂), 5.42 (dd, J = 17.2 Hz, 2.0 Hz, 1H, C<u>H</u>=CH₂), 5.23 (dd, J = 9.8 Hz, 0.7 Hz, 1H, CH=C<u>H</u>₂), 3.72 (m, 4H, CH₂-O), 3.60 (m, 4H, CH₂-O), 3.48 (m, 4H, CH₂-O), 3.21 (dd, J = 7.0 Hz, 2.2 Hz, 1H, -CHO-C<u>H</u>O-CH), 3.01 (ddt, J = 3.0 Hz, 3.4 Hz, 2.3 Hz, 1H, CH₂-C<u>H</u>O-CHO), 0.88 (s, 9H, C(CH₃)₃), 0.05 (s, 6H, Si(CH₃)₂).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 134.8$ (CH₂=<u>C</u>H-), 119.6 (CH₂=), 72.51 (CH₂-O), 70.67 (CH₂-O), 70.53 (CH₂-O), 62.57 (CH₂-O), 58.6 (CH-O), 56.0 (CH-O), 26.1 (C(<u>C</u>H₃)₃), 18.5 (<u>C</u>(CH₃)₃), -5.10 (Si(CH₃)₂).

2-[2-(3-Vinyl-oxiranylmethoxy)-ethoxy]-ethanol (67)

The synthesis proceeded according to **GP8** with 2.35 g (7.8 mmol) vinylepoxide **65** in 200 ml methanol and 3.51 g (94.9 mmol) ammoniumfluoride. The crude product was used without further purification.

Yield: 0.88 g (4.7 mmol, 60%) yellowish oil GC-MS(DB_100): $t_R = 3.94$ min

¹H-NMR (400 MHz, CDCl₃) : $\delta = 5.61$ (m, 1H, CH=C<u>H</u>₂), 5.46 (dd, J = 17.2 Hz, 1.8 Hz, 1H, C<u>H</u>=CH₂), 5.25 (d, 1H, CH=C<u>H</u>₂), 3.79 (dd, J = 11.7 Hz, 2.9 Hz, 2H, CH₂-O), 3.64 (m, 6H, CH₂-O), 3.48 (dd, 4H, J = 11.7 Hz, 5.7 Hz, CH₂-O), 3.24 (dd, J = 7.0 Hz, 2.2 Hz, 1H, -CHO-C<u>H</u>O-CH), 3.06 (ddt, J = 5.5 Hz, 3.1 Hz, 2.3 Hz, 1H, CH₂-C<u>H</u>O-CHO).

¹³C-NMR (100 MHz, CDCl₃): δ = 134.6 (CH₂=<u>C</u>H-), 119.7 (CH₂=), 72.43 (CH₂-O), 70.95 (CH₂-O), 70.71 (CH₂-O), 70.29 (CH₂-O), 61.65 (CH₂-O), 58.55 (CH-O), 55.89 (CH-O).

2-{2-[2-(3-Vinyl-oxiranylmethoxy)-ethoxy]-ethoxy}-ethanol (68)

The synthesis proceeded according to **GP8** with 3.20 g (10.1 mmol) vinylepoxide **66** in 150 ml methanol and 4.28 g (115.7 mmol) ammoniumfluoride. The crude product was used without further purification.

 $R_f = 0.34$ (cyclohexane:ethylacetate 20:1)

Yield: 0.88 g (4.7 mmol, 60%) yellowish oil

GC-MS(DB_100): $t_R = 4.26 \min [M]^+ = 201$

¹H-NMR (400 MHz, CDCl₃) : δ = 5.61 (m, 2H, CH=C<u>H</u>₂), 5.46 (dd, *J* = 17.2 Hz, 1.8 Hz, 1H, C<u>H</u>=CH₂), 5.25 (d, 1H, CH=C<u>H</u>₂), 3.79 (dd, *J* = 11.7 Hz, 2.9 Hz, 2H, CH₂-O), 3.64 (m, 6H, CH₂-O), 3.48 (dd, 4H, *J* = 11.7 Hz, 5.7 Hz, CH₂-O), 3.24 (dd, *J* = 7.0 Hz, 2.2 Hz, 1H, -C<u>H</u>O_{epox}-CH), 3.06 (ddt, *J* = 5.5 Hz, 3.1 Hz, 2.3 Hz, 1H, CH₂-C<u>H</u>O_{epox}).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 134.6$ (CH₂=<u>C</u>H-), 119.7 (CH₂=), 72.43 (CH₂-O), 70.95 (CH₂-O), 70.71 (CH₂-O), 70.29 (CH₂-O), 61.65 (CH₂-O), 58.55 (CH-O), 55.89 (CH-O).

7,7-Bis-(phenylsulfonyl)-heptanoic acid 5-(3-vinyl-oxiranyl)-pentylester (8)

The synthesis proceeded according to **GP9** with 0.31 g (2.0 mmol) alcohol **5** in 10 ml DCM and 0.90 g (2.2 mmol) acid **7** in 10 ml DCM, 0.01 g (0.1 mmol) DMAP and 0.42 g (2.2 mmol) EDC. The crude product was purified via flash chromatography (silica, flashstation, cyclohexane:ethylacetate 1:1).

 $R_{\rm f}\,{=}\,0.33$

Yield: 0.72 g (4.6 mmol, 63%) yellowish oil

¹H-NMR (400 MHz, CDCl₃) : δ = 7.88-7.85 (m, 4H, ar. H), 7.62-7.60 (m, 2H, ar. H), 7.51-7.48 (m, 4H, ar. H), 5.40-5.17 (br m, 3H, olefin. H), 4.40 (t, *J* = 6 Hz, 1 H, CH(SO₂Ph)₂), 4.04-3.98 (m, 2H, CH₂COO), 3.04-3.03 (m, 1H, CHO_{epox}), 2.76-2.75 (m, 1H, CHO_{epox}), 2.20-2.16 (m, 2H, alk. CH₂), 2.11-2.08 (m, 2H, alk. CH₂), 1.60-1.17 (m, 14H, alk. CH₂).

¹³C-NMR (100 MHz, CDCl₃) : δ = 172.9 (COO), 137.5 (ar. C), 135.4 (all. C), 134.2 (ar. C), 129.1 (ar. C), 128.7 (ar. C), 118.6 (all. C), 83.05 (CH(SO₂Ph)₂), 63.98 (<u>C</u>H₂COO), 60.11 (CHO_{epox}), 60.00 (CHO_{epox}), 33.75 (alk. C), 31.64 (alk. C), 28.39 (alk. C), 28.28 (alk. C), 27.46 (alk. C), 25.60 (alk. C), 25.41 (alk. C), 25.26 (alk. C), 24.07 (alk. C), 20.92 (alk. C), 14.12 (<u>C</u>H₂CH(SO₂Ph)₂)

HRMS (FAB, 3-NBA) for $C_{28}H_{37}O_7S_2$ [M+H]⁺: calcd.: 549.1981 found: 549.2001

found: 549.

HPLC (C18): t_R= 9.96 min

7,7-Bis-(phenylsulfonyl)-heptanoic acid 9-(3-vinyl-oxiranyl)-nonylester (10)

The synthesis proceeded according to **GP9** with 0.95 g (4.5 mmol) 9-(3-vinyl-oxiranyl)-nonan-1-ol (**60**) in 20 ml DCM and 2.0 g (4.9 mmol) 7,7-bis-(phenylsulfonyl)-heptanoic acid (**7**) in 20 ml DCM, 0.1 g (0.9 mmol) DMAP and 0.94 g (4.9 mmol) EDC. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:1).

 $R_f = 0.41$ (cyclohexane:ethylacetate 3:1)

Yield: 0.91 g (1.5 mmol, 33%) yellowish oil

¹H-NMR (400 MHz, CDCl₃) : δ = 7.96-7.94 (m, 4H, ar. H), 7.72-7.68 (m, 2H, ar. H), 7.60-7.55 (m, 4H, ar. H), 5.75-5.23 (br m, 3H, olefin. H), 4.38 (t, *J* = 5.7 Hz, 1 H, CH(SO₂Ph)₂), 4.05 (t, *J* = 6.7 Hz, 2H, CH₂COO), 3.09 (dd, *J* = 2.1 Hz, 7.4 Hz, 1H, CHO_{epox}), 2.82 (dt, *J* = 2.3 Hz, 5.5 Hz, 1H, CHO_{epox}), 2.25 (t, *J* = 7.5 Hz, 2H, alk. CH₂), 2.18-2.13 (m, 2H, alk. CH₂), 1.63-1.54 (m, 8H, alk. CH₂), 1.38-1.27 (m, 12H, alk.H).

¹³C-NMR (100 MHz, CDCl₃) : δ = 173.2 (COO), 137.7 (ar. C), 135.7 (all. C), 134.4 (ar. C), 129.4 (ar. C), 128.9 (ar. C), 118.7 (all. C), 83.56 (CH(SO₂Ph)₂), 64.52 (<u>C</u>H₂COO), 60.49 (CHO_{epox}), 58.75 (CHO_{epox}), 34.06 (alk. C), 32.05 (alk. C), 29.48 (alk. C), 29.31 (alk. C), 28.73 (alk. C), 28.57 (alk. C), 27.84 (alk. C), 26.00 (alk. C), 25.53 (alk. C), 24.35 (alk. C).

HPLC (C18): t_R= 11.34 min

7,7-Bis-(phenylsulfonyl)-heptanoic acid 2-[2-(3-vinyl-oxiranylmethoxy)-ethoxy]ethylester (12)

The synthesis proceeded according to **GP9** with 0.82 g (4.4 mmol) 2-[2-(3-vinyl-oxiranylmethoxy)ethoxy]-ethanol (**67**) in 5 ml DCM and 2.0 g (4.8 mmol) 7,7-bis-(phenylsulfonyl)-heptanoic acid (**7**) in 5 ml DCM, 0.1 g (0.9 mmol) DMAP and 0.92 g (4.8 mmol) EDC. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:2).

 $R_f = 0.32$ (cyclohexane:ethylacetate 3:2)

Yield: 0.93 g (1.6 mmol, 37%) yellowish oil

¹H-NMR (400 MHz, CDCl₃) : δ = 7.96-7.94 (m, 4H, ar. H), 7.72-7.68 (m, 2H, ar. H), 7.60-7.56 (m, 4H, ar. H), 5.69-5.28 (br m, 3H, olefin. H), 4.38 (t, *J* = 5.7 Hz, 1 H, CH(SO₂Ph)₂), 4.24-4.22 (m, 2H, CH₂COO), 3.80 (dd, *J* = 11.7 Hz, 3.1 Hz, 1H, CH₂-glycol chain), 3.71-3.65 (m, 6H, -CH₂-glycol chain), 3.51 (dd, *J* = 5.5 Hz, 11.7 Hz, 1H, CH₂-glycol chain), 3.27 (dd, *J* = 7.2 Hz, 2.2 Hz, 1H, CHO_{epox}), 3.08 (ddd, *J* = 2.3 Hz, 5.4 Hz, 3.1 Hz, 1H, CHO_{epox}), 2.28 (t, *J* = 7.4 Hz, 2H, alk. CH₂), 2.18-2.13 (m, 2H, alk. CH₂), 1.63-1.54 (m, 4H, alk. CH₂), 1.32-1.27 (m, 2H, alk.H).

¹³C-NMR (100 MHz, CDCl₃) : δ = 173.1 (COO), 137.7 (ar. C), 134.8 (all. C), 134.4 (ar. C), 129.4 (ar. C), 129.0 (ar. C), 119.7 (all. C), 83.53 (CH(SO₂Ph)₂), 71.05 (CH₂-glycol chain), 70.77 (CH₂- glycol chain), 70.56 (CH₂-glycol chain), 69.20 (CH₂-glycol chain), 63.45 (<u>C</u>H₂COO), 58.66 (CHO_{epox}), 55.97 (CHO_{epox}), 33.88 (alk. C), 28.50 (alk. C), 27.81 (alk. C), 25.52 (alk. C), 24.25 (alk. C).

HRMS (FAB, 3-NBA) for $C_{28}H_{37}O_9S_2$ [M+H]⁺: calcd.: 581.1879 found: 581.1908

HPLC (C18): t_R= 8.85 min

7,7-Bis-(phenylsulfonyl)-heptanoic acid 2-{2-[2-(3-vinyl-oxiranylmethoxy)-ethoxy]ethoxy}-ethylester (14)

The synthesis proceeded according to **GP9** with 0.14 g (0.61 mmol) $2-\{2-[2-(3-vinyl-oxiranylmethoxy)-ethoxy]-ethoxy\}-ethanol ($ **68**) in 2.5 ml DCM and 0.28 g (0.67 mmol) 7,7-bis-(phenylsulfonyl)-heptanoic acid (**7**) in 2.5 ml DCM, 0.01 g (0.1 mmol) DMAP and 0.13 g (0.67 mmol) EDC. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:2).

 $R_f = 0.31$ (cyclohexane:ethylacetate 3:2)

Yield: 0.23 g (0.37 mmol, 60%) colorless oil

¹H-NMR (400 MHz, CDCl₃) : δ = 7.95-7.93 (m, 4H, ar. H), 7.71-7.67 (m, 2H, ar. H), 7.59-7.55 (m, 4H, ar. H), 5.73-5.27 (br m, 3H, olefin. H), 4.38 (t, *J* = 5.7 Hz, 1 H, CH(SO₂Ph)₂), 4.22 (t, *J* = 4.9 Hz, 2H, CH₂COO), 3.78 (dd, *J* = 11.7 Hz, 3.1 Hz, 1H, CH₂-glycol chain), 3.71-3.64 (m, 10H, -CH₂-glycol chain), 3.50 (dd, *J* = 5.5 Hz, 11.7 Hz, 1H, CH₂-glycol chain), 3.26 (dd, *J* = 7.2 Hz, 2.3 Hz, 1H, CHO_{epox}), 3.07 (ddd, *J* = 2.2 Hz, 5.4 Hz, 3.2 Hz, 1H, CHO_{epox}), 2.27 (t, *J* = 7.4 Hz, 2H, alk. CH₂), 2.15-2.11 (m, 2H, alk. CH₂), 1.59-1.53 (m, 4H, alk. CH₂), 1.28-1.23 (m, 2H, alk.H).

¹³C-NMR (100 MHz, CDCl₃) : δ = 173.1 (COO), 137.6 (ar. C), 134.7 (all. C), 134.4 (ar. C), 129.4 (ar. C), 128.9 (ar. C), 119.7 (all. C), 83.47 (CH(SO₂Ph)₂), 70.98 (CH₂-glycol chain), 70.75 (CH₂-glycol chain), 70.58 (CH₂-glycol chain), 69.13 (CH₂-glycol chain), 63.46 (<u>C</u>H₂COO), 58.63 (CHO_{epox}), 55.96 (CHO_{epox}), 33.84 (alk. C), 28.46 (alk. C), 27.77 (alk. C), 25.49 (alk. C), 24.21 (alk. C).

HRMS (FAB, 3-NBA) for $C_{30}H_{40}O_{10}S_2Na \ [M+Na]^+$: calcd.: 647.1961

found.: 647.1968

HPLC (C18): t_R= 8.88 min

2-Hydroxy-benzoic acid 5-(3-vinyl-oxiranyl)-pentylester (55)

A 25 ml 2-neck flask equipped with a 10 ml-dropping funnel was dried in vacuum and filled with argon. 50 mg (6,7-Epoxy)-8-nonen-1-ol (**5**) (0.32 mmol) and 126 mg triphenylphosphine (1.5 eq, 0.48 mmol) were added to the flask and dissolved in 3 ml abs. THF. The a solution of 97 mg DIAD (1.5 eq, 0.48 mmol) in 2 ml abs. THF was added dropwise within 1 min. After 20 min a solution of 44 mg salicylic acid (1 eq, 0.32 mmol) in 2 ml abs. THF was added dropwise, and the reaction mixture was stirred at RT for 12 h. The reaction mixture was taken up on silica and put on a silica column to perform purification via flash chromatography (eluent: ethylacetate:cyclohexane 1:1).

 $R_{f} \approx 0.92$ (EA:CH 1:1)

Yield: 67 mg (0.24 mmol, 75%), slightly turbid, colorless oil

¹H-NMR (400 MHz, CDCl₃): $\delta = 10.81$ (s, 1H, -O<u>H</u>), $\delta = 7.83$ (dd, J = 8.0/1.8 Hz, 1H, H-6), 7.44 (m, 1H, H-5), 6.97 (dd, J = 8.4, 1.0 Hz, 1H, H-3), 6.96 (m, 1H, H-4), 5.76-5.22 (m, 3H, R-C<u>H</u>=C<u>H</u>₂), 4.34 (t, J = 6.7 Hz, 2H, R-COO-C<u>H</u>₂), 3.10 (dd, J = 7.4, 2.2 Hz, 1H, epoxide-H α to C=C), 2.83 (m, 1H, epoxide-H α to alkylchain), 1.80 (td, J = 13.3, 6.7 Hz, 2H, R-COO-CH₂C<u>H</u>₂-R`), 1.52 (m, 6H, alkyl-H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 169.9$ (-<u>C</u>OOR), 161.4 (<u>C</u>_{arom}-OH), 135.6 (R-<u>C</u>H=CH₂), 135.4 (C-4), 132.3 (C-6), 129.7 (C-5), 120.3 (C-1), 118.9 (C-3), 117.4 (R-CH=<u>C</u>H₂), 65.2 (RCOO<u>C</u>H₂R'), 60.2 (epoxide-C α to C=C), 58.6 (epoxide-C α to alkylchain), 31.9 (alkyl-C), 28.6 (alkyl-C), 25.9 (Alkyl-C), 25.8 (alkyl-C)

2-[7,7-Bis-(phenylsulfonyl)-heptanoyloxy])-benzoic acid 5-(3-vinyl-oxiranyl)-pentylester (56)

The synthesis proceeded according to **GP9** with 61.0 mg **55** (0.22 mmol) in 2 ml DCM, 99.0 mg 7,7bis(phenylsulfonyl)-heptanoic acid (**7**) (0.24 mmol), 6.0 mg DMAP (0.05 mmol) and 37.5 μ l DIC (0.24 mmol). The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 1:1).

 $R_f \approx 0.62$ (cyclohexane:ethylacetate 1:1) Yield: 47 mg (0.07 mmol, 32%), colorless oil HPLC (C18): t_R=10.54 min

¹H-NMR (400 MHz, CDCl₃): $\delta = 8.00$ (dd, J = 7.7 Hz, 1.7 Hz, 1H, H-6), 7.96 (dd, J = 8.5 Hz, 1.3 Hz, 4H, H_{arom} *o*-sulfonyl), 7.70 (m, 2H, H_{ar} *p*-sulfonyl), 7.57 (m, 5H, H_{ar} *m*-sulfonyl u. H-4), 7.31 (td, J = 7.6 Hz, 1.1 Hz, 1H, H-5), 7.09 (dd, J = 8.0Hz, 1.2 Hz, 1H, H-3), 5.75-5.22 (m, 3H, R-C<u>H</u>=C<u>H</u>₂), 4.43 (t, J = 5.7 Hz, 1H, R-C<u>H</u>(-SO₂R')₂), 4.25 (t, J = 6.7 Hz, 2H, R-COO-C<u>H</u>₂R'), 3.10 (m, 1H, epoxide-H α to C=C), 2.83 (m, 1H, epoxid-H α to alkylchain), 2.59 (t, J = 7.4 Hz, 2H, R_{ar}-OOC-C<u>H</u>₂R'), 2.19 (m, 2H, R-C<u>H</u>₂CH(O₂S-R')₂), 1.57 (m, 14H, alkyl-H)

¹³C-NMR (100 MHz, CDCl₃): δ = 172.1 (R_{ar}-OO<u>C</u>R'), 164.6 (R_{ar}-<u>C</u>OOR'), 150.9 (<u>C</u>_{ar}-OH), 140.6 (R-<u>C</u>H=CH₂ u. R₂<u>C</u>SO₂R'), 136.1 (C_{ar}), 134.8 (C_{ar}), 134.0 (C_{ar}), 132.8 (C_{ar}), 131.8 (C_{ar}), 129.9 (C_{ar}), 126.2 (C_{ar}), 124.1 (C_{ar}), 123.8 (C_{ar}), 120.8 (C_{ar}), 119.3 (R-CH=<u>C</u>H₂), 83.8 (R-<u>C</u>H(SO₂Ph)₂), 65.4 (R_{ar}COO<u>C</u>H₂R'), 60.7 (epoxid-C α to C=C), 59.1 (epoxid-C α to alkylchain), 34.3 (alkyl-C), 32.3 (alkyl-C), 29.1 (alkyl-C), 28.8 (alkyl-C), 28.2 (alkyl-C), 26.3 (alkyl-C), 26.1 (alkyl-C), 25.9 (alkyl-C), 24.4 (alkyl-C)

HRMS (FAB, 3-NBA) for
$$C_{35}H_{40}O_9S_2Na [M+Na]^+$$
: calcd.: 691.2011
found: 691.2004

(E)-8,8-Bis-(phenylsulfonyl)-12-hydroxy-1-oxacycloheptadec-10-en-2-one (9)

The synthesis was performed according to **GP10** with 17.3 mg (0.009 mmol) Pd-resin **1a/Pd** in 1.1 ml abs. THF and 49.8 mg (0.09 mmol) substrate **8** in 1.1 ml abs. THF. The crude product was taken up in acetonitrile for the purification via prep. HPLC. The corresponding *Z*-Isomer was not observed. Yield: 33.5 mg (0.0603 mmol, 67%) colorless crystalls

¹H-NMR (400 MHz, CDCl₃) : $\delta = 8.02$ -8.00 (m, 4H, ar. H), 7.70-7.68 (m, 2H, ar. H), 7.60-7.57 (m, 4H, ar. H), 5.87 (dt, J = 14.3 Hz, 7.4 Hz, 1H, olefin. H), 5.63 (dd, J = 15.3 Hz, 7.1 Hz 1 H, olefin. H), 4.22-4.17 (m, 1H, CHOH), 4.12-4.00 (m, 2H, CH₂COO), 3.09-2.95 (m, 2H, CH₂C(SO₂Ph)₂), 2.37-2.22 (m, 2H, CH₂C(SO₂Ph)₂), 2.20-2.02 (m, 2H, alk. H), 1.74-1.19 (m, 14H, alk. H).

¹³C-NMR (100 MHz, CDCl₃) : δ = 173.0 (COO), 139.3 (ar. C), 136.6 (ar. C), 134.4 (ar. C), 131.0 (alk. C), 130.97 (alk. C), 128.5 (ar. C), 123.2 (ar. C), 91.12 (C(SO₂Ph)₂), 72.37 (CHOH), 64.14 (CH₂COO), 37.41 (alk. C), 34.72 (alk. C), 32.03 (alk. C), 29.59 (alk. C), 29.13 (alk. C), 28.73 (alk. C), 26.74 (alk. C), 25.21 (alk. C), 24.73 (alk. C), 23.20 (alk. C).

HRMS (FAB, 3-NBA) for $C_{28}H_{36}O_7S_2Na [M+Na]^+$:		571.1800
	found:	571.1776

HPLC (C18): t_R= 8.72 min

(E)-8,8-Bis-(phenylsulfonyl)-12-hydroxy-1-oxacycloheneicosan-10-en-2-one (11)

The synthesis proceeded according to **GP10** with 16.0 mg (0.008 mmol) Pd-resin **1a/Pd** in 1.0 ml abs. THF and 50.0 mg (0.083 mmol) substrate **10** in 1.0 ml abs. THF. The crude product was taken up in acetonitrile for the purification via prep. HPLC. The corresponding *Z*-Isomer was not observed.

Yield: 23.1 mg (0.038 mmol, 46%) colorless crystalls

¹H-NMR (400 MHz, CDCl₃) : $\delta = 8.05$ -8.03 (m, 4H, ar. H), 7.74-7.70 (m, 2H, ar. H), 7.62-7.58 (m, 4H, ar. H), 6.13-5.32 (m, 2H, olefin. H), 4.18-4.12 (m, 2H, CH₂COO), 3.52 (m, 1H, CHOH), 3.16-2.96 (m, 2H, CH₂C(SO₂Ph)₂), 2.32-2.23 (m, 2H, CH₂C(SO₂Ph)₂), 2.21-2.01 (m, 2H, alk. H), 1.86-1.21 (m, 22H, alk. H).

¹³C-NMR (100 MHz, CDCl₃) : δ = 173.4 (COO), 138.8 (ar. C), 136.5 (ar. C), 136.3 (ar. C), 134.5 (ar. C), 131.7 (all. C), 131.1 (all. C), 128.5 (ar. C), 123.0 (ar. C), 91.05 (C(SO₂Ph)₂), 72.69 (CHOH), 63.99 (CH₂COO), 36.82 (alk. C), 34.74 (alk. C), 33.50 (alk. C), 31.81 (alk. C), 31.50 (alk. C), 30.01 (alk. C), 29.17 (alk. C), 28.85 (alk. C), 28.31 (alk. C), 27.87 (alk. C), 25.00 (alk. C), 23.40 (alk. C), 22.74 (alk. C).

HRMS (FAB, 3-NBA) for $C_{32}H_{44}O_7S_2 [M]^+$:	calcd.:	604.2528
	found:	604.2581

HPLC (C18): t_R= 10.55 min

(E)-8,8-Bis-(phenylsulfonyl)-12-hydroxy-1,14,17-trioxacyclononadecan-10-en-2-one (13)

The synthesis proceeded according to **GP10** with 16.5 mg (0.009 mmol) Pd-resin **1a/Pd** in 1.0 ml abs. THF and 50.0 mg (0.086 mmol) substrate **12** in 1.0 ml abs. THF. The crude product was taken up in acetonitrile for the purification via prep. HPLC. The corresponding *Z*-Isomer was not observed.

Yield: 16.3 mg (0.028 mmol, 33%) colorless crystalls

¹H-NMR (400 MHz, CDCl₃) : $\delta = 8.03-8.01$ (m, 4H, ar. H), 7.72-7.68 (m, 2H, ar. H), 7.60-7.56 (m, 4H, ar. H), 6.03 (dt, J = 15.2 Hz, 6.9 Hz, 1H, olefin. H), 5.68 (dd, J = 15.5 Hz, 6.2 Hz, 1H, olefin. H), 4.31-4.27 (m, 1H, CHOH), 4.22 (t, J = 5.7 Hz, 2.7 Hz, 2H, CH₂COO), 3.81-3.76 (m, 1H, CH₂-glycol chain), 3.72-3.60 (m, 6H, CH₂-glycol chain), 3.47 (dd, J = 7.1 Hz, 10.4 Hz, 1H, CH₂-glycol chain), 3.07-3.04 (m, 2H, CH₂C(SO₂Ph)₂), 2.36-2.29 (m, 2H, CH₂C(SO₂Ph)₂), 2.17-2.08 (m, 2H, alk. H), 1.78-1.70 (m, 2H, alk. H), 1.69-1.59 (m, 2H, alk. H), 1.34-1.27 (m, 2H, alk. H).

¹³C-NMR (100 MHz, CDCl₃) : δ = 173.2 (COO), 136.5 (ar. C), 136.3 (ar. C), 135.2 (ar. C), 134.4 (ar. C), 131.0 (ar. C), 128.4 (all. C), 124.2 (ar. C), 91.25 (C(SO₂Ph)₂), 75.30 (CHOH), 71.42 (CH₂-glycol

chain), 70.91 (CH₂-glycol chain), 69.07 (CH₂-glycol chain), 63.48 (<u>C</u>H₂COO), 33.79 (alk. C), 31.60 (alk. C), 28.79 (alk. C), 28.27 (alk. C), 23.81 (alk. C), 22.16 (alk. C).

HRMS (FAB, 3-NBA) for $C_{28}H_{36}O_9S_2Na \ [M+Na]^+$: calcd.: 603.1698 found: 603.1728

HPLC (C18): t_R= 7.85 min

(*E*)-8,8-Bis-(phenylsulfonyl)-12-hydroxy-1,14,17,20-tetraoxacyclodocosan-10-en-2-one (15)

The synthesis proceeded according to **GP10** with 15.4 mg (0.008 mmol) Pd-resin **1a/Pd** in 1.0 ml abs. THF and 50.0 mg (0.080 mmol) substrate **14** in 1.0 ml abs. THF. The crude product was taken up in acetonitrile for the purification via prep. HPLC. The corresponding *Z*-Isomer was not observed.

Yield: 26.6 mg (0.043 mmol, 53%) colorless oil

¹H-NMR (400 MHz, CDCl₃) : $\delta = 8.05$ -8.00 (m, 4H, ar. H), 7.73-7.69 (m, 2H, ar. H), 7.60-7.56 (m, 4H, ar. H), 6.00 (dt, J = 15.4 Hz, 6.9 Hz, 1H, olefin. H), 5.74 (dd, J = 15.4 Hz, 6.2 Hz, 1H, olefin. H), 4.31-4.27 (m, 1H, CHOH), 4.24 (t, J = 4.3 Hz, 2H, CH₂COO), 3.72-3.60 (m, 11H, CH₂-glycol chain), 3.47 (dd, J = 6.2 Hz, 10.2 Hz, 1H, CH₂-glycol chain), 3.07 (ddd, J = 7.5 Hz, 16.2 Hz, 26.1 Hz, 2H, CH₂C(SO₂Ph)₂), 2.36-2.30 (m, 2H, CH₂C(SO₂Ph)₂), 2.20-2.12 (m, 2H, alk. H), 1.77-1.60 (m, 4H, alk. H), 1.36-1.25 (m, 2H, alk. H).

¹³C-NMR (100 MHz, CDCl₃) : δ = 173.3 (COO), 136.6 (ar. C), 136.5 (ar. C), 135.0 (ar. C), 134.4 (ar. C), 131.1 (all. C), 128.4 (all. C), 124.0 (arom. C), 91.43 (C(SO₂Ph)₂), 75.02 (CHOH), 70.95 (CH₂-glycol chain), 70.66 (CH₂-glycol chain), 70.54 (CH₂-glycol chain), 70.33 (CH₂-glycol chain), 69.16 (CH₂-glycol chain), 63.43 (<u>C</u>H₂COO), 33.56 (alk. C), 31.44 (alk. C), 29.05 (alk. C), 28.26 (alk. C), 23.85 (alk.C), 22.21 (alk. C).

HRMS (FAB, 3-NBA) for $C_{30}H_{40}O_{10}S_2Na [M+Na]^+$:	calcd.:	647.1961
	found:	647.1932

HPLC (C18): t_R= 7.94 min

(*E*)-Benzo-8,8-bis-(phenylsulfonyl)-12-hydroxy-1,18-dioxacycloheneicosan-10-en-2,19dion (69)

The synthesis proceeded according to **GP10** with 21.0 mg (0.011 mmol) Pd-resin **1a/Pd** in 1.38 ml abs. THF and 70.0 mg (0.11 mmol) substrate **56** in 1.38 ml abs. THF. After 20 h at 50°C the conversion was determined by HPLC to be 69%. After another 12 h at 50 °C conversion reached 78%.

The crude product was taken up in acetonitrile for the purification via prep. HPLC. The corresponding *Z*-Isomer was not observed.

Yield: 53.0 mg (0.08 mmol, 40%) colorless oil

¹H-NMR (400 MHz, CDCl₃): $\delta = 8.05-8.03$ (m, 4H, H_{ar} *o*-sulfonyl), 7.98 (dd, J = 7.8 Hz, 1.8 Hz, 1H, ar. H), 7.73-7.69 (m, 2H, H_{ar} *p*-sulfonyl), 7.60 (t, J = 7.9 Hz, 4H, H_{ar} *m*-sulfonyl), 7.54 (ddd, J = 8.0 Hz, 7.4 Hz, 1.8 Hz, 1H, H-4), 7.31 (td, J = 7.6 Hz, 1.2 Hz, 1H, ar. H), 7.06 (dd, J = 8.0 Hz, 1.0 Hz, 1H, ar. H), 5.94 (dt, J = 14.9 Hz, 6.9 Hz, 1H, R-CHOH-CH=CH-R'), 5.67 (dd, J = 15.4 Hz, 6.9 Hz 1H, R-CHOH-CH=CH-R'), 4.30-4.26 (m, 2H, R-COO-CH₂R'), 3.03 (m, 2H, R-CHOHR'), 2.59 (t, J = 7.5 Hz, 2H, R_{ar}-OOC-CH₂R'), 2.16 (m, 2H, R-CH₂CR'(O₂S-Ph)₂), 1.90 (m, 2H, alkyl-H), 1.70 (m, 6H, alkyl-H), 1.56 (m, 2H, alkyl-H), 1.35 (m, 6H, alkyl-H),

¹³C-NMR (100 MHz, CDCl₃): $\delta = 171.6$ (R_{ar}-OO<u>C</u>R'), 165.5 (R_{ar}-<u>C</u>OOR'), 149.8 (RR'<u>C</u>-OH), 139.6 (R-<u>C</u>H=CHR' u. R₂<u>C</u>SO₂R'), 136.7 (C_{ar}), 134.6 (C_{ar}), 133.6 (C_{ar}), 131.9 (C_{ar}), 131.2 (C_{ar}), 128.6 (C_{ar}), 126.0 (C_{ar}), 124.3 (C_{ar}), 123.5 (C_{ar}), 123.1 (R-CH=<u>C</u>H₂), 100.0 (R-<u>C</u>(SO₂Ph)₂), 72.5 (R<u>C</u>HOHR'), 65.4 (R_{ar}COO<u>C</u>H₂R'), 36.9 (alkyl-C), 33.9 (alkyl-C), 32.3 (alkyl-C), 30.0 (alkyl-C), 29.2 (alkyl-C), 28.7 (alkyl-C), 25.7 (alkyl-C), 24.9 (alkyl-C), 24.0 (alkyl-C), 23.4 (alkyl-C)

HPLC (C18): t_R=9.67 min

calcd.:	369.2192
found:	369.2152
cacld.:	391.2011
found	391 1985
	calcd.: found: cacld.: found:

Experiments realated to Sonogashira-reactions

General procedure for ester saponification (GP11)

To a solution of 1 eq. ester in MeOH are added tetrahydrofurane, H_2O and 7 eq. NaOH. The reaction mixture is heated under reflux overnight. The solvents are removed in vaccuo using a rotovap. The residue is extracted with 100 ml ethylacetate and 40 ml dest. H_2O . After phase separation the organic layer is discarded, the aqueous layer is set to pH 1 by addition of 5% HCl, and then extracted with 3x150 ml ethylacetate. The combined organic layers are dried over Na_2SO_4 and then concentrated in vaccuo using a rotovap.

General procedure for the methylation of an ω -amino acid (GP12)

A flask is charged with abs. MeOH and cooled in an ice bath to 0°C. Over a period of 30 min 2.2 eq thionylchloride are slowly added and stirred for further 20 min. Then 1 eq acid are added, and the reaction mixture stirred for 10 min at 0°C and 3 h at RT. The solvents are removed in vaccuo using a rotovap and the residue recrystallized from ethylacetate:cyclohexane:methanol.

General procedure for carbodiimide-mediated amide formation (GP13)

To a solution of 1.0 eq acid, 1.0 eq triethylamine and 1.0 eq alcohol in CH_2Cl_2 are added 1.0 eq DIC and 1.1 eq HOBt at 0°C. The reaction mixture is stirred overnight at RT and then washed with H₂O (3x10 ml), NaHCO₃-solution (3x10 ml) and brine (3x10 ml). The crude product is purified via flash chromatography.

General procedure for acid chloride-mediated amide formation (GP14)

To a solution of 1 eq amine and 1 eq acid chloride in DCM cooled to 0°C are added dropwise 1.05 eq triethylamine. The reaction mixture is stirred overnight at RT. The solvents are removed in vaccuo using a rotovap and the crude product is purified via flash chromatography.

General procedure for sulfonamide formation (GP15)

To a solution of 1.0 eq amine in $CHCl_3$:*N*-methylmorpholine (5:1) are added 1.1 eq sulfonylchloride at RT. The reaction mixture is stirred overnight at RT and then washed with H₂O (1x10 ml) and brine (1x10 ml). The crude product is purified via flash chromatography.

General procedure for the esterification of isatoic anhydride (GP16)

In an oven dried flask 1.0 eq isatoic anhydride, 2.0 eq alcohol, 1 eq DMAP in abs. DMF are heated to 60° C for 24 h. After cooling to RT the reaction mixture is washed with H₂O. The aqueous layer is

extracted 3x with ethylacetate. The combined organic layers are dried over Na_2SO_4 , the solvents are removed in vaccuo using a rotovap and the crude product is purified via flash chromatography.

General procedure for intramolecular Sonogashira-reactions (GP17)

An inert Schlenk flask is charged with Pd-beads or $Pd[PPh_3]_4$ (0.1 eq Pd). After 3 vacuum/argon cycles the beads are swollen in degassed dioxane:piperidine (2:1). 0.1 eq CuI are added and the reaction mixture is heated to 60°C. The substrate, dissolved in dioxane:piperidine (2:1), is added. The reaction is heated at 60 °C overnight. The reaction is monitored by HPLC. After complete conversion (15 h) the reaction mixture is cooled to RT.

In reactions with Pd-beads the beads are filtered off, washed with DCM (1x45 ml, 10 min), with DCM:MeOH 1:1 (2x20 ml, 2x10min) and with DCM (1x20 ml, 10 min).

Die collected filtrates in the reaction with Pd-resin or the reaction mixture in the reactions with $Pd[PPh_3]_4$ are washed with brine (1x20 ml). The aqueous layer is extracted with DCM (3x30 ml). The combined organic layers are dried over Na_2SO_4 , the solvents are removed in vaccuo using a rotovap and the crude product is purified via flash chromatography or via prep. HPLC (C4).

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12-Hydroxydodecanoic acid (16)

The synthesis proceeded according to **GP11** with 9.32 g dodecanelactone (47.0 mmol), 3.8 g NaOH (94.0 mmol) and 120 ml MeOH:THF: H_2O (2.5:2.5:1)

Yield: 10.16 g (47.0 mmol, quant.) colorless crystals

mp: 83.5°C

¹H-NMR (400 MHz, CDCl₃): δ = 3.54 (t, J =6.7 Hz, 2H,-C<u>H</u>₂OH), 2.27 (t, J =7.4 Hz, 2H, -C<u>H</u>₂COOH), 1.62-1.51 (m, 4H, alk.H), 1.38-1.31 (m, 14H, alk.H)

The analytical data are in accordance to literature.^{vii}

12-(tert-Butyl-dimethyl-silanyloxy)-dodecanoic acid (17)

In a dried flask are added to a solution of 500.0 mg (1 eq, 2.31 mmol) 12-hydroxydodecanoic acid (**16**) and 236.2 mg (2 eq, 3.47 mmol) imidazole in 5 ml abs. DMF 348.2 mg (1.5 eq, 2.31 mmol) TBDMSCl. The reaction mixture is stirred at RT for 24 h and then washed with 5 ml H₂O. The aqueous layer is extracted with Et_2O (3x 5 ml). The combined organic layers are washed with 10% NaHCO₃ solution, dried over Na₂SO₄. The solvents are removed in vaccuo using a rotovap. The crude product is purified via flash chromatography.

 $R_f = 0.32$ (CH:EA 3:1)

Yield: 379.1 mg (1.15 mmol, 50 %) colorless oil GC-MS(DB_100): $t_R = 6.05$ min

¹H-NMR (400 MHz, CDCl₃): δ = 3.59 (t, *J* =6.6 Hz, 2H, -C<u>H</u>₂O-), 2.33 (t, *J* =7.5 Hz, 2H, -C<u>H</u>₂COOH), 1.64-1.60 (m, 2H, alk.H), 1.51-1.48 (m, 2H, alk.H), 1.34-1.25 (m, 14H, alk.H), 0.89 (s, 12H, -C(CH₃)₃), 0.04 (s, 6H, -Si(CH₃)₂)

The analytical data are in accordance to literature.

12-(tert-Butyl-dimethyl-silanyloxy)-dodecanoic acid hex-5-inyl-ester (18)

The synthesis proceeded according to **GP9** with 100.0 mg (0.30 mmol) 12-(*tert*-butyl-dimethyl-silanyloxy)-dodecanoic acid (**17**), 26.5 mg (0.27 mmol) 1-hexinol, 57.4 mg (0.30 mmol) EDC, 6.7 mg (0.055 mmol) DMAP and 5 ml DCM. The crude product is purified via flash chromatography (silica, CH:EA 20:1).

$$\label{eq:Rf} \begin{split} R_{\rm f} &= 0.42 \; ({\rm CH:EA} \; 20{:}1) \\ \mbox{Yield: } 92.0 \; \mbox{mg} \; (0.22 \; \mbox{mmol}, \; 83\%) \; \mbox{colorless oil} \\ \mbox{GC-MS(DB_100): } t_{\rm R} &= 6.31 \; \mbox{min} \end{split}$$

¹H-NMR (400 MHz, CDCl₃): δ = 4.08 (t, *J* =6.4 Hz, 2H, -CH₂OOC-), 3.59 (t, *J* =6.5 Hz, 2H, -C<u>H₂O-Si-</u>), 2.28 (t, *J* =7.5 Hz, 2H, -CH₂COO), 2.23 (dt, *J* =7.0 Hz, 2.7 Hz, 2H, -C<u>H₂CCH</u>), 1.95 (t, *J* =2.6 Hz, 1H, -CCH), 1.77-1.71 (m, 2H, alk.H), 1.64-1.57 (m, 4H, alk.H), 1.51-1.48 (m, 2H, alk.H), 1.31-1.26 (m, 16H, alk.H), 0.89 (s, 12H, -C(CH₃)₃), 0.04 (s, 6H, -Si(CH₃)₂)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.6$ (-COO), 83.80 (-<u>C</u>CH), 68.69 (-C<u>C</u>H), 63.67 (-<u>C</u>H₂OOC), 63.33 (-CH₂OSi), 34.42 (-CH₂COO), 32.97 (alk.C), 29.69 (alk.C), 29.62 (alk.C), 29.53 (alk.C), 29.53 (alk.C), 29.35 (alk.C), 29.25 (alk.C), 27.80 (alk.C), 26.09 (alk.C), 25.90 (alk.C), 25.06 (alk.C), 18.50 (alk.C), 18.19 (alk.C), -5.073 (-Si(CH₃)₂)

12-Hydroxy-dodecanoic acid hex-5-inyl-ester (72)

The synthesis proceeded according to **GP8** with 100.0 mg (0.24 mmol) 12-(*tert*-butyl-dimethyl-silanyloxy)-dodecanoic acid hex-5-inyl-ester (**18**), 103.8 mg (2.80 mmol) NH₄F and 6 ml methanol. Yield: 80.6 mg (0.27 mmol, quant.) colorless oil GC-MS(DB_100): $t_R = 5.70$ min

¹H-NMR (400 MHz, CDCl₃): δ = 4.08 (t, *J* =6.4Hz, 2H, -CH₂OOC-), 3.63 (t, *J* =6.6Hz, 2H, -CH₂O-Si-), 2.28 (t, *J* =7.5Hz, 2H, -CH₂COO), 2.23 (dt, *J* =7.0Hz, 2.6 Hz, 2H, - CH₂CCH), 1.96 (t, *J* =2.6 Hz, 1H, -CCH), 1.77-7.73 (m, 2H, alk.H), 1.63-1.54 (m, 6H, alk.H), 1.33-1.17 (m, 16H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.7$ (-COO), 83.83 (-<u>C</u>CH), 68.68 (-C<u>C</u>H), 63.69 (-<u>C</u>H₂OOC), 63.06 (-CH₂OSi), 34.42 (-CH₂COO), 32.86 (alk.C), 29.63 (alk.C), 29.56 (alk.C), 29.49 (alk.C), 29.31 (alk.C), 29.22 (alk.C), 27.79 (alk.C), 25.82 (alk.C), 25.06 (alk.C), 18.19 (alk.C)

12-(2-lodbenzoyl)-dodecanoic acid hex-5-inyl-ester (19)

The synthesis proceeded according to **GP9** with 296.2 mg (1.0 mmol) 12-hydroxy-dodecanoic acid hex-5-inyl-ester (**72**), 272.8 mg (1.1 mmol) 2-iodobenzoic acid, 210.3 mg (1.1 mmol) EDC, 24.4 mg (0.2 mmol) DMAP and 10 ml DCM. The crude product was purified via flash chromatography (silica, CH:EA 3:1).

R_f = 0.69 (CH:EA 3:1) Yield: 438.9 mg (0.83 mmol, 83%) colorless oil

HPLC (C4): $t_R = 7.92 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.98 (dd, *J* =8.0 Hz, 1.0 Hz, 1H, ar.H), 7.77 (dd, *J* =7.8 Hz. 1.8 Hz, 1H, ar.H), 7.39 (dt, *J* =7.6 Hz, 1,2 Hz, 1H, ar.H), 7.14 (dt, *J* =7.6 Hz, 1.8 Hz, 1H, ar.H), 4.33 (t, *J* =6.7 Hz, 2H, -CH₂OOC-Ar), 4.09 (t, *J* =6.5, 2H, CH₂OOC-), 2.29 (t, *J* =7.7 Hz, 2H, -CH₂COO), 2.23 (dt, *J* =7.0 Hz, 2.7 Hz, 2H, - C<u>H₂CCH</u>), 1.96 (t, *J* =2.6 Hz, 1H, -CCH), 1.79-1.72 (m, 4H, alk.H), 1.63-1.58 (m, 4H, alk.H), 1.46-1.42 (m, 2H, alk.H), 1.33-1.25 (m, 12H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.6$ (-COO), 166.5 (Ar-COO), 141.1 (ar.C), 132.3 (2 ar.C), 130.6 (ar.C), 127.7 (ar.C), 93.85 (C_{arom}-I), 83.87 (-<u>C</u>CH), 68.67 (-C<u>C</u>H), 65.86 (-<u>C</u>H₂OOC-Ar), 63.67 (-<u>C</u>H₂OOC), 34.43 (-CH₂COO), 29.53 (alk.C), 28.68 (alk.C), 27.80 (alk.C), 26.15 (alk.C), 25.07 (alk.C), 18.21 (alk.C)

HRMS (FAB, 3-NBA) for $C_{24}H_{33}NO_3 [M+H]^+$:	calcd.:	527.1658
	found:	527.1691
for C ₂₄ H ₃₃ NO ₃ Na [M+Na] ⁺ :	calcd.:	549.1478
	found:	549.1496

12-(4-lodbenzoyl)-dodecanoic acid hex-5-inyl-ester (73)

The synthesis proceeded according to **GP9** with 296.2 mg (1.0 mmol) 12-hydroxy-dodecanoic acid hex-5-inyl-ester (**72**), 272.8 mg (1.1 mmol) 4-iodobenzoic acid, 210.3 mg (1.1 mmol) EDC, 24.4 mg (0.2 mmol) DMAP and 10 ml DCM. The crude product was purified via flash chromatography (silica, CH:EA 3:1).

R_f = 0.79 (CH:EA 3:1) Yield: 454.1 mg (0.86 mmol, 86%) colorless oil

HPLC (C4): $t_R = 8.18 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.81-7.78 (m, 2H, ar.H), 7.75-7.72 (m, 2H, ar.H), 4.30 (t, *J* =6.6 Hz, 2H, -CH₂OOC-Ar), 4.09 (t, *J* =6.4, 2H, CH₂OOC-), 2.29 (t, *J* =7.5 Hz, 2H, -CH₂COO), 2.23 (dt, *J* =7.0 Hz, 2.5 Hz, 2H, - C<u>H₂</u>CCH), 1.96 (t, *J* =2.6 Hz, 1H, -CCH), 1.79-1.72 (m, 4H, alk.H), 1.64-1.56 (m, 4H, alk.H), 1.45-1.38 (m, 2H, alk.H), 1.36-1.28 (m, 12H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.6$ (-COO), 165.9 (Ar-COO), 137.5 (ar.C), 130.8 (2 ar.C), 129.8 (2 ar.C), 100.4 (C_{arom}-I), 83.84 (-<u>C</u>CH), 68.69 (-C<u>C</u>H), 65.41 (-<u>C</u>H₂OOC-Ar), 63.70 (-<u>C</u>H₂OOC), 34.44 (-CH₂COO), 29.59 (alk.C), 29.58 (alk.C), 29.52 (alk.C), 29.35 (alk.C), 29.26 (alk.C), 28.77 (alk.C), 27.83 (alk.C), 26.11 (alk.C), 25.10 (alk.C), 25.08 (alk.C), 18.22 (alk.C)

HRMS (FAB, 3-NBA) for $C_{24}H_{33}NO_3 [M+H]^+$:	calcd.:	527.1658
	found:	527.1686

for $C_{24}H_{33}NO_3Na \ [M+Na]^+$: calcd.: 549.1478 found: 549.1495

6-Aminohexanoic acid methylester (74)

The synthesis proceeded according to **GP12** with 15 ml methanol, 2.4 (33.4 mmol) thionylchloride and 2.0 g (15.2 mmol) 6-aminocaproic acid.

Yield: 2.50 g (15.2 mmol, quant.) colorless crystals

mp.: 120-121°C

¹H-NMR (400 MHz, CDCl₃): δ = 8.26 (br s, 2H, -NH₂), 3.66 (s, 3H, -OMe), 3.02 (m, 2H, -C<u>H₂NH₂)</u>, 2.33 (t, *J* =6.8 Hz, 2H, -CH₂COO-), 1.81 (m, 2H, alk.H), 1.66 (t, *J* =6.5Hz, 2H, alk.H), 1.45-1.41 (m, 2H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): δ = 173.9 (-COO), 51.60 (-OMe), 43.13 (-CH₂NH₂), 33.61 (-<u>C</u>H₂COOund alk.C), 27.23 (alk.C), 25.89 (alk.C), 24.16 (alk.C)

The analytical data are in accordance to literature.^{viii}

6-(4-lodobenzamido)-hexanoic acid methylester (76)

The synthesis proceeded according to **GP13** with 1.19 g (4.8 mmol) 4-iodobenzoic acid, 0.7 g (4.8 mmol) 6-aminohexanoic acid methylester (**74**), 0.67 ml (4.8 mmol) triethylamine, 0.75 ml (4.8 mmol) DIC and 809.0 mg (5.3 mmol) HOBt. The crude product was purified via flash chromatography (silica, CH:EA 3:1).

R_f = 0.43 (CH:EA 3:1) Yield: 1.14 g (3.03 mmol, 63%) colorless crytals

¹H-NMR (400 MHz, CDCl₃): δ = 7.78-7.76 (m, 2H, ar.H), 7.50-7.48 (m, 2H, ar.H), 6.25 (br s, 1H, - NH-), 3.66 (s, 3H, -OMe), 3.44 (dt, *J* = 5.9 Hz, 7.1 Hz, 2H, -C<u>H</u>₂-NHCO-), 2.33 (t, *J* = 7.3 Hz, 2H, - CH₂COO-), 1.71-1.59 (m, 4H, alk.H), 1.44-1.38 (m, 2H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 174.3$ (-COO-), 166.9 (-CONH-), 138.0 (2 ar.C), 134.4 (\underline{C}_{arom} -CONH-), 128.7 (2 ar.C), 98.46 (\underline{C}_{arom} -I), 51.79 (-OMe), 39.99 (CH₂-NHCO-), 34.00 (\underline{C} H₂-COO-), 29.36 (alk.C), 26.55 (alk.C), 24.53 (alk.C)

6-(2-lodobenzamido)-hexanoic acid methylester (75)

The synthesis proceeded according to **GP13** with 1.19 g (4.8 mmol) 2-iodobenzoic acid, 0.7 g (4.8 mmol) 6-aminohexanoic acid methylester (**74**), 0.67 ml (4.8 mmol) triethylamine, 0.75 ml (4.8 mmol)

DIC and 809.0 mg (5.3 mmol) HOBt. The crude product was purified via flash chromatography (silica, CH:EA 3:1).

 $R_{f} = 0.36 (CH:EA 3:1)$

Yield: 1.20 g (3.20 mmol, 67%) colorless solid

¹H-NMR (400 MHz, CDCl₃): δ = 7.82-7.79 (m, 1H, ar.H), 7.33-7.32 (m, 2H, ar.H), 7.05 (ddd, *J* = 7.9 Hz, 3.9 Hz, 5.3 Hz, 1H, ar.H), 6.02 (brs, 1H, -NH), 3.63 (s, 3H, -OMe), 3.39 (dt, *J* = 6.5 Hz, 6.6 Hz, 2H, -CH₂NHCO-), 2.30 (t, *J* = 7.3 Hz, 2H, -CH₂COO-), 1.68-1.58 (m, 4H, alk.H), 1.45-1.39 (m, 2H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.9$ (-COO), 169.3 (-CONH-), 142.4 (- \underline{C}_{arom} CONH-), 139.7 (ar.C), 130.9 (ar.C), 128.1 (ar.C), 128.0 (ar.C), 92.37 (\underline{C}_{arom} -I), 51.45 (-OMe), 39.71 (- \underline{C} H₂-NHCO-), 33.78 (- \underline{C} H₂-COO-), 28.96 (alk.C), 26.39 (alk.C), 24.40 (alk.C)

6-(4-lodbenzenesulfonyl)-hexanoic acid methylester (83)

The synthesis proceeded according to **GP15** with 0.70 g (4.8 mmol) 6-aminohexanoic acid methylester (**74**) and 1.68 g (5.3 mmol) pipsylchloride in 19 ml NMM:CHCl₃-solution. The crude product is purified via flash chromatography (silica, CH:EA 3:1).

$R_{f} = 0.46 (CH:EA 3:1)$

Yield: 1.06 g (2.59 mmol, 54%) colorless solid

¹H-NMR (400 MHz, CDCl₃): δ = 7.87 (d, J = 8.4 Hz, 2H, ar.H), 7.57 (d, J = 8.4 Hz, 2H, ar.H), 4.56 (br s, 1H, -NH-), 3.66 (s, 3H, -OMe), 2.96-2.95 (m, 2H, -C<u>H</u>₂NHCO-), 2.27 (t, J = 7.3 Hz, 2H, -CH₂COO-), 1.57 (dt, J = 15.3 Hz, 7.6 Hz, 2H, alk.H), 1.49 (dt, J = 14.8 Hz, 7.4 Hz, 2H, alk.H), 1.34-1.26 (m, 2H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): δ = 174.2 (-COO-), 139.9 (-<u>C</u>_{ar}-CONH-), 138.6 (2 ar.C), 128.7 (2 ar.C), 98.70 (-C_{ar}-I), 51.83 (-OMe), 43.18 (-<u>C</u>H₂NHCO), 33.91 (-<u>C</u>H₂COO-), 29.45 (alk.C), 26.11 (alk.C), 24.35 (alk.C)

6-(4-lodbenzamido)-hexanoic acid (78)

The synthesis proceeded according to **GP11** with 187.5 mg (0.5 mmol) 6-(4-iodobenzamido)-hexanoic acid methylester (**76**), 146.0 mg (3.6 mmol) NaOH and 10 ml MeOH: H_2O (1:1).

Yield: 169.9 mg (0.47 mmol, 95%) colorless solid

¹H-NMR (400 MHz, CDCl₃): δ = 7.67-7.65 (m, 2H, ar.H), 7.42-7.40 (m, 2H, ar.H), 6.25 (br s, 1H, - NH-), 3.28 (t, *J* = 7.1 Hz, 2H, -C<u>H</u>₂-NHCO-), 2.21 (t, *J* = 7.3 Hz, 2H, -CH₂-COO-), 1.58-1.48 (m, 4H, alk.H), 1.34-1.28 (m, 2H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 176.2$ (-COO-), 167.4 (-CONH-), 137.4 (2 ar.C), 133.7 (- \underline{C}_{ar} -CONH-), 128.5 (ar.C), 128.4 (ar.C), 98.00 (- \underline{C}_{ar} -I), 39.52 (- \underline{C}_{H_2} NHCO-), 33.59 (- \underline{C}_{H_2} COO-), 28.66 (alk.C), 26.10 (alk.C), 24.16 (alk.C)

6-(2-lodobenzamido)-hexanoic acid (77)

The synthesis proceeded according to **GP11** with 1.2 g (3.2 mmol) 6-(2-iodobenzamido)-hexanoic acid methylester (**75**), 897.0 mg (22.4 mmol) NaOH and 60 ml MeOH: H_2O (1:1).

Yield: 1.14 g (3.16 mmol, 99%) colorless solid

¹H-NMR (400 MHz, CDCl₃): δ = 7.89-7.87 (m, 1H, ar. H), 7.43 (dt, *J* = 1.2 Hz, 7.5 Hz, 1H, ar.H), 7.32 (dd, *J* = 1.7 Hz, 7.7 Hz, 1H, ar.H), 7.17-7.13 (m, 1H, ar.H), 4.92 (br s, 1H, -NH-), 3.37-3.33 (m, 2H, -C<u>H</u>₂-NHCO-), 2.32 (t, *J* = 7.3 Hz, 2H, -C<u>H</u>₂COO-), 1.70-1.62 (m, 4H, alk.H), 1.52-1.46 (m, 2H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 177.5$ (-COO), 172.5 (-CONH), 144.2 (-<u>C</u>_{ar}-CONH-), 140.7 (ar.H), 131.9 (ar.H), 129.2 (ar.H), 128.8 (ar.C), 93.25 (-C_{ar}-I), 40.66 (-<u>C</u>H₂NHCO-), 34.81 (-<u>C</u>H₂COO-), 29.84 (alk.C), 27.59 (alk.C), 25.69 (alk.C)

6-(4-lodobenzenesulfonyl)-hexanoic acid (84)

The synthesis proceeded according to **GP11** with 1.02g (2.49 mmol) 6-(4-iodobenzenesulfonyl)hexanoic acid methylester (**83**), 698.0 mg (17.4 mmol) NaOH and 50 ml MeOH: H_2O (1:1).

Yield: 925.9 mg (2.33 mmol, 94%) colorless solid

¹H-NMR (400 MHz, CDCl₃): δ = 7.95-7.93 (m, 2H, ar.H), 7.59-7.57 (m, 2H, ar.H), 2.85 (t, *J* = 6.9 Hz, 2H, -C<u>H</u>₂-NHCO-), 2.24 (t, *J* = 7.3 Hz, 2H, -CH₂-COO-), 1.54 (tt, *J* = 7.5 Hz, 7.6 Hz, 2H, alk.H), 1.46 (tt, *J* = 7.0 Hz, 7.5 Hz, 2H, alk.H), 1.34-1.28 (m, 2H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): δ = 177.5 (-COO), 141.8 (-C_{ar}-SO₂-), 139.6 (2 ar.C), 129.5 (2 ar.C), 100.2 (-C_{ar}-I), 43.84 (-<u>C</u>H₂NHSO₂-), 34.72 (-<u>C</u>H₂COO-), 30.31 (alk.C), 27.11 (alk.C), 25.52 (alk.C)

2-Aminobenzoic acid hex-5-inyl-ester (87)

The synthesis proceeded according to **GP16** with 507.0 mg (2.5 mmol) isatoic anhydride, 500.0 mg (5.0 mmol) 1-hexinol, 305.0 mg (2.5 mmol) DMAP and 20 ml DMF. The crude product was purified via flash chromatography (silica, CH:EA 3:1).

 $R_f = 0.66 (CH:EA 3:1)$

Yield: 426.3 mg (1.96 mmol, 70%) yellowish oil

¹H-NMR (400 MHz, CDCl₃): δ = 7.86 (ddd. *J* = 8.1 Hz, 1.5 Hz, 0.3 Hz, 1H, ar.H), 7.27 (ddd, *J* = 8.4 Hz, 6.9 Hz, 1.6 Hz, 1H, ar.H), 6.68-6.63 (m, 2H, ar.H), 5.73 (br s, 2H, -NH₂), 4.30 (t, *J* = 6.5 Hz, 2H, -CH₂OOC-), 2.28 (dt, *J* = 7.0 Hz, 2.7 Hz, 2H, -CH₂CCH), 1.98 (t, *J* = 2.6 Hz, 1H, -CCH), 1.93-1.86 (m, 2H, alk.H), 1.74-1.68 (m, 2H, alk.H).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 169.1$ (-COO), 150.3 (-C_{ar}NH₂), 134.0 (ar.C), 131.1 (ar.C), 116.7 (ar.C), 116.3 (ar.C), 111.0 (-C_{ar}-COO), 83.88 (-CCH), 68.74 (-CCH), 63.75 (-CH₂OOC), 27.77 (alk.C), 25.06 (alk.C), 18.10 (alk.C)

2-Aminobenzoic aicd undec-10-inyl-ester (88)

The synthesis proceeded according to **GP16** with 1.0 g (5.5 mmol) isatoic anhydride, 1.85 g (11.0 mmol) 1-undecinol, 672.0 mg (5.5 mmol) DMAP and 40 ml DMF. The crude product was purified via flash chromatography (silica, CH:EA 3:1).

 $R_{f} = 0.57 (CH:EA 3:1)$

Yield: 481.2 mg (1.70 mmol, 30%) colorless oil

¹H-NMR (400 MHz, CDCl₃): δ = 7.87 (dd. *J* = 8.0 Hz, 1.0 Hz, 1H, ar.H), 7.28-7.24 (m, 1H, arom.H), 6.68-6.63 (m, 2H, ar.H), 5.71 (br s, 2H, -NH₂), 4.26 (t, *J* = 6.6 Hz, 2H, -CH₂OOC-), 2.18 (dt, *J* = 7.1 Hz, 2.6 Hz, 2H, -C<u>H₂</u>CCH), 1.94 (t, *J* = 2.6 Hz, 1H,-CCH), 1.75 (tt, *J* = 7.2 Hz, 7.0 Hz, 2H, alk.H), 1.52 (tt, *J* = 7.4 Hz, 7.3 Hz, 2H, alk.H), 1.45-1.36 (m, 5H, alk.H), 1.35-1.31 (m, 5H, alk.H).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 168.2$ (-COO), 150.2 (-C_{ar}NH₂), 133.9 (ar.C), 131.2 (ar.C), 116.7 (ar.C), 116.3 (ar.C), 111.2 (-C_{ar}-COO), 84.73 (-CCH), 68.06 (-CCH), 64.44 (-CH₂OOC), 29.33 (alk.C), 29.18 (alk.C), 28.98 (alk.C), 28.69 (alk.C), 28.67 (alk.C), 28.42 (alk.C), 26.03 (alk.C), 18.36 (alk.C)

6-(4-lodobenzamido)-hexanoic acid hex-5-inyl-ester (81)

The synthesis proceeded according to **GP9** with 216.6 mg (0.6 mmol) 6-(4-iodobenzamido)-hexanoic acid (**78**), 58.9 mg (0.6 mmol) 1-hexinol, 36.7 mg (0.3 mmol) DMAP, 83.1 mg (0.66 mmol) DIC and 5 ml DCM. The crude product was purified via prep. HPLC.

Yield: 222.4 mg (0.50 mmol, 84%) colorless solid

HPLC (C4): $t_R = 7.92 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.78 (d, *J* = 8.6 Hz, 2H, ar.H), 7.48 (d, *J* = 8.6 Hz, 2H, ar.H), 6.41 (br s, 1H, -NH-), 4.09 (t, *J* = 6.5 Hz, 2H, -CH₂-OOC-), 3.46 (dt, *J* = 6.3 Hz, 6.8 Hz, 2H, -C<u>H₂-NHCO-</u>), 2.33 (t, *J* = 7.3 Hz, 2H, -CH₂-COO-), 2.23 (dt, *J* = 2.6 Hz, 7.0 Hz, 2H, -C<u>H₂CCH</u>), 1.96 (t, *J* = 2.7 Hz, 1H, -CCH), 1.79-1.71 (m, 2H, alk.H), 1.70-1.55 (m, 6H, alk.H), 1.45-1.37 (m, 2H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): δ = 174.1 (-COO), 169.1 (-CONH), 138.1 (2 ar.C), 134.3 (<u>C</u>_{ar}-CONH), 128.8 (2 ar.C), 98.94 (-C_{ar}-I), 84.05 (-<u>C</u>CH), 69.00 (-C<u>C</u>H), 64.20 (-<u>C</u>H₂-OOC-), 40.23 (-<u>C</u>H₂NHCO), 34.18 (-<u>C</u>H₂COO), 29.12 (alk.C), 27.87 (alk.C), 26.46 (alk.C), 25.15 (alk.C), 24.42 (alk.C), 18.29 (alk.C)

 $\begin{array}{ll} \mbox{HRMS (FAB, 3-NBA) for $C_{19}H_{25}INO_3$ [M+H]^+:} & \mbox{calcd.: } 442.0879 \\ & \mbox{found: } 442.0867 \\ \\ \mbox{for $C_{19}H_{24}INO_3Na$ [M+Na]^+:} & \mbox{calcd.: } 464.0699 \\ & \mbox{found: } 464.0695 \end{array}$

6-(2-lodobenzamido)-hexanoic acid hex-5-inyl-ester (79)

The synthesis proceeded according to **GP9** with 216.6 mg (0.6 mmol) 6-(2-iodebenzamido)-hexanoic acid (**77**), 58.9 mg (0.6 mmol) 1-hexinol, 36.7 mg (0.3 mmol) DMAP, 83.1 mg (0.66 mmol) DIC and 5 ml DCM. The crude product was purified via prep. HPLC.

Yield: 172.2 mg (0.39 mmol, 65%) colorless solid

HPLC (C4): $t_R = 7.62 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.82 (d, *J* = 7.82 Hz, 1H, ar.H), 7.34 (d, *J* = 4.1 Hz, 2H, arom.H), 7.06 (dt, *J* = 7.9 Hz, 4.6 Hz, 1H, ar.H), 5.95 (br s, 1H, -NH-), 4.06 (t, *J* = 6.5 Hz, 2H, -CH₂OOC-), 3.42 (dt, *J* = 7.4 Hz, 6.2 Hz, 2H, -C<u>H₂NHCO</u>), 2.30 (t, *J* = 7.3 Hz, 2H, -CH₂COO), 2.21 (dt, *J* = 2.7 Hz, 7.0 Hz, 2H, -C<u>H₂-CCH</u>), 1.94 (t, *J* = 2.6 Hz, 1H, -CCH), 1.77-1.71 (m, 2H, alk.H), 1.70-1.62 (m, 4H, alk.H), 1.61-1.53 (m, 2H, alk.H), 1.47-1.39 (m, 2H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.6$ (-COO), 169.4 (-CONH), 142.4 (- \underline{C}_{ar} -CONH), 139.7 (ar.C), 130.9 (ar.C), 128.1 (ar.C), 128.0 (ar.C), 92.37 (- \underline{C}_{ar} -I), 83.80 (- \underline{C} CH), 68.70 (-C<u>C</u>H), 63.76 (-<u>C</u>H₂OOC), 39.75 (-<u>C</u>H₂NHCO), 34.03 (-<u>C</u>H₂COO), 29.00 (alk.C), 27.60 (alk.C), 26.42 (alk.C), 24.87 (alk.C), 24.44 (alk.C), 18.00 (alk.C)

HRMS (FAB, 3-NBA) for $C_{19}H_{25}INO_3 [M+H]^+$: calcd.: 442.0879 found: 442.0856 for $C_{19}H_{24}INO_3Na [M+Na]^+$: calcd.: 464.0699 found: 464.0719

6-(4-lodobenzenesulfonyl)-hexanoic acid hex-5-inyl-ester (85)

The synthesis proceeded according to **GP9** with 198.5 mg (0.5 mmol) 6-(4-iodobenzenesulfonyl)hexanoic acid (**84**), 49.8 mg (0.5 mmol) 1-hexinol, 12.2 mg (0.1 mmol) DMAP, 69.4 mg (0.55 mmol) DIC and 5 ml DCM. The crude product was purified via prep. HPLC.

Yield: 158.5 mg (0.33 mmol, 66%) colorless solid

HPLC (C4): $t_R = 9.02 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.88-7.86 (m, 2H, ar.H), 7.58-7.56 (m, 2H, ar.H), 4.62 (t, *J* = 6.1 Hz, 1H, -NH-), 4.08 (t, *J* = 6.5 Hz, 2H, -CH₂OOC-), 2.95 (dt, *J* = 6.6 Hz, 6.5 Hz, 2H, -C<u>H₂NHCO-), 2.26 (t, *J* = 7.2 Hz, 2H, -CH₂COO), 2.23 (dt, *J* = 2.7 Hz, 6.9 Hz, 2H, -C<u>H₂CCH), 1.96 (t, *J* = 2.6 Hz, 1H, -CCH), 1.78-1.71 (m, 2H, alk.H), 1.62-1.55 (m, 4H, alk.H), 1.49 (tt, *J* = 7.6 Hz, 7.3 Hz, 2H, alk.H), 1.34-1.28 (m, 2H, alk.H)</u></u>

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.5$ (-COO), 139.7 (-C_{ar}-SO₂), 138.3 (2 ar.C), 128.4 (2 ar.C), 99.88 (-C_{ar}-I), 83.85 (-<u>C</u>CH), 68.75 (-C<u>C</u>H), 63.86 (-<u>C</u>H₂OOC), 42.93 (-CH₂NHSO₂), 33.88 (-CH₂COO), 29.21 (alk.C), 27.64 (alk.C), 25.88 (alk.C), 24.91 (alk.C), 24.13 (alk.C), 18.05 (alk.C)

2-lodobenzoylamido-benzoic acid hex-5-inyl-ester (89)

The synthesis proceeded according to **GP14** with 193.2 mg (0.89 mmol) 2-aminobenzoic acid hex-5-inyl-ester (**87**), 244.4 mg (0.89 mmol) 2-iodobenzoyl chloride, 90.0 mg (0.93 mmol) triethylamine and 1.5 ml DCM. The crude product was purified via flash chromatography (silica, CH:EA 3:1).

 $R_{\rm f} = 0.46 \; (CH:EA \; 3:1)$

Yield: 354.2 mg (0.79 mmol, 89%), yellowish oil

HPLC (C4): $t_R = 9.41 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 11.40 (br s, 1H, -NH-), 8.89 (d, *J* = 8.6 Hz, 1H, ar.H), 8.08 (dd, *J* = 8.0 Hz, 1.4 Hz, 1H, ar.H), 7.94 (dd, *J* = 7.8 Hz, 1.0 Hz, 1H, ar.H), 7.62 (ddd, *J* = 8.6 Hz, 7.3 Hz, 1.4 Hz, 1H, ar.H), 7.56 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H, ar.H), 7.45 (dt, *J* = 7.5Hz, 1.2 Hz, 1H, ar.H), 7.15 (dddd, *J* = 7.9 Hz, 7.5 Hz, 4.2 Hz, 1.3 Hz, 2H, ar.H), 4.32 (t, *J* = 6.5 Hz, 2H, -CH₂OOC-), 2.27 (dt, *J*

= 7.0 Hz, 2.6 Hz, 2H, -C<u>H</u>₂CCH), 1.97 (t, *J* = 2.6 Hz, 1H,-CCH), 1.90 (tt, *J* = 7.7 Hz, 6.6 Hz, 2H, alk.H), 1.71-1.66 (m, 4H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): δ = 168.1 (-COO), 167.6 (-CONH), 142.0 (-<u>C</u>_{arom}CONH-), 141.2 (-<u>C</u>_{ar}NHCO), 140.4 (ar.C), 134.7 (ar.C), 131.4 (ar.C), 130.8 (ar.C), 128.3 (ar.C), 128.0 (ar.C), 123.1 (ar.C), 120.6 (ar.C), 115.6 (-<u>C</u>_{ar}COO), 92.69 (-C_{ar}-I), 83.62 (-<u>C</u>CH), 68.92 (-C<u>C</u>H), 64.94 (-<u>C</u>H₂OOC), 27.53 (alk.C), 24.92 (alk.C), 18.05 (alk.C)

4-lodobenzoylamido-benzoic acid hex-5-inyl-ester (91)

The synthesis proceeded according to **GP14** with 325.6 mg (1.50 mmol) 2-aminobenzoic acid hex-5-inyl-ester (**87**), 407.9 mg (1.50 mmol) 4-iodobenzoylchloride, 159.4 mg (1.57 mmol) triethylamine and 2.5 ml DCM. The crude product was purified via flash chromatography (silica, CH:EA 3:1).

 $R_f = 0.42$ (CH:EA 3:1)

Yield: 356.2 mg (0.80 mmol, 53%), colorless solid

HPLC (C4): $t_R = 9.21 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): $\delta = 12.09$ (br s, 1H, -NH-), 8.89 (d, J = 8.4 Hz, 1H, ar.H), 8.09 (d, J = 8.0 Hz, 1H, ar.H), 7.87 (d, J = 8.2 Hz, 1H, ar.H), 7.79-7.75 (m, 3H, ar.H), 7.61 (t, J = 8.1 Hz, 1H, ar.H), 7.14 (t, J = 7.9, Hz, 1H, ar.H), 4.39 (t, J = 6.4 Hz, 2H, -CH₂OOC-), 2.30 (dt, J = 6.9 Hz, 2.6 Hz, 2H, -CH₂CCH), 1.99 (t, J = 2.6 Hz, 1H, -CCH), 1.75-1.68 (m, 4H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 168.6$ (-COO), 164.9 (-CONH), 141.7 (- \underline{C}_{arom} NHCO), 138.0 (ar.C), 137.7 (ar.C), 134.8 (ar.C), 134.3 (ar.C), 131.0 (ar.C), 130.9 (ar.C), 128.9 (ar.C), 122.8 (ar.C), 120.4 (ar.C), 115.3 (- \underline{C}_{ar} COO), 99.19 (- C_{ar} -I), 83.64 (- \underline{C} CH), 68.95 (- $C\underline{C}$ H), 65.06 (- \underline{C} H₂OOC), 27.57 (alk.C), 24.95 (alk.C), 18.08 (alk.C)

6-(4-lodobenzamido)-hexanoic acid undec-10-inyl-ester (82)

The synthesis proceeded according to **GP9** with 216.6 mg (0.6 mmol) 6-(4-iodobenzamido)-hexanoic acid (**78**), 100.9 mg (0.6 mmol) 1-undecinol, 36.7 mg (0.3 mmol) DMAP, 83.1 mg (0.66 mmol) DIC and 5 ml DCM. The crude product was purified via prep. HPLC.

Yield: 192.2 mg (0.38 mmol, 63%) colorless solid

HPLC (C4): $t_R = 9.17 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.76 (d, *J* = 8.4 Hz, 2H, ar.H), 7.49 (d, *J* = 8.4 Hz, 2H, ar.H), 6.27 (br s, 1H, -NH-), 4.04 (t, *J* = 6.7 Hz, 2H, -CH₂OOC-), 3.44 (dt, *J* = 4.7 Hz, 11.7 Hz, 2H, -CH₂NHCO-

), 2.31 (t, *J* = 7.3 Hz, 2H, -CH<u>2</u>COO), 2.17 (dt, *J* = 2.5 Hz, 6.9 Hz, 2H, -C<u>H</u>₂CCH), 1.93 (t, *J* = 2.63, 1H, -CCH), 1.70-1.58 (m, 6H, alk.H), 1.56-1.48 (m, 2H, alk.H), 1.44-1.37 (m, 4H, alk.H), 1.33-1.25 (m, 8H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.7$ (-COO), 166.7 (-CONH), 137.7 (2 ar.C), 134.1 (-<u>C</u>_{ar}CONH-), 128.5 (2 ar.C), 98.20 (-C_{ar}-I), 84.72 (-<u>C</u>CH), 68.07 (-C<u>C</u>H), 64.52 –<u>C</u>H₂OOC), 39.74 (-<u>C</u>H₂NHCO), 34.02 (-<u>C</u>H₂COO), 29.31 (alk.C), 29.14 (alk.C), 29.07 (alk.C), 28.97 (alk.C), 28.66 (alk.C), 28.58 (alk.C), 28.42 (alk.C), 26.29 (alk.C), 25.86 (alk.C), 24.29 (alk.C), 18.36 (alk.C)

HRMS (FAB, 3-NBA) for $C_{24}H_{35}INO_3 [M+H]^+$: calcd.: 512.1662 found: 512.1690

6-(2-lodobenzamido)-hexanoic acid undec-10-inyl-ester (80)

The synthesis proceeded according to **GP9** with 216.6 mg (0.6 mmol) 6-(2-iodobenzamido)-hexanoic acid (**77**), 100.9 mg (0.6 mmol) 1-undecinol, 36.7 mg (0.3 mmol) DMAP, 83.1 mg (0.66 mmol) DIC and 5 ml DCM. The crude product was purified via prep. HPLC.

Yield: 268.1 mg (0.52 mmol, 87%) colorless solid

HPLC (C4): $t_R = 8.95 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): $\delta = 7.85$ (d, J = 7.8 Hz, 1H, ar.H), 7.38-7.36 (m, 2H, ar.H), 7.10 (ddd, J = 8.0 Hz, 3.8 Hz, 5.4 Hz, 1H, ar.H), 6.00 (br s, 1H, -NH-), 4.04 (t, J = 6.7Hz, 2H, -CH₂OOC-), 3.46 (dt, J = 6.2 Hz, 6.8 Hz, 2H, -C<u>H</u>₂NHCO), 2.32 (t, J = 7.3 Hz, 2H, -CH₂COO-), 2.17 (dt, J = 2.4 Hz, 7.0 Hz, 2H, -C<u>H</u>₂CCH), 1.93 (t, J = 2.6, 1H, -CCH), 1.72-1.63 (m, 4H, alk.H), 1.62-1.57 (m, 2H, alk.H), 1.55-1.50 (m, 2H, alk.H), 1.48-1.40 (m, 2H, alk.H), 1.39-1.34 (m, 2H, alk.H), 1.30-1.27 (m, 8H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.8$ (-COO), 170.1 (-CONH-), 141.8 (ar.H), 139.8 (ar.H), 131.2 (ar.H), 128.3 (ar.H), 128.2 (ar.H), 92.28 (-C_{ar}-I), 84.72 (-<u>C</u>CH), 68.07 (-C<u>C</u>H), 64.60 (-<u>C</u>H₂OOC), 40.03 (-<u>C</u>H₂NHCO), 34.10 (-<u>C</u>H₂COO), 29.31 (alk.C), 29.13 (alk.C), 28.97 (alk.C), 28.89 (alk.C), 28.66 (alk.C), 28.57 (alk.C), 28.42 (alk.C), 26.42 (alk.C), 25.85 (alk.C), 24.44 (alk.C), 18.35 (alk.C)

HRMS (FAB, 3-NBA) for $C_{24}H_{35}INO_3 [M+H]^+$:	calcd.:	512.1662
	found:	512.1647
for C ₂₄ H ₃₄ INO ₃ Na [M+Na] ⁺ :	calcd.:	534.1481
	found:	534.1508

6-(4-lodobenzenesulfonyl)-hexanoic acid undec-10-inyl-ester (86)

The synthesis proceeded according to **GP9** with 198.5 mg (0.5 mmol) 6-(4-iodobenzenesulfonyl)hexanoic acid (**84**), 84.1 mg (0.5 mmol) 1-undecinol, 12.2 mg (0.1 mmol) DMAP, 69.4 mg (0.55 mmol) DIC and 5 ml DCM. The crude product was purified via prep. HPLC.

Yield: 144.3 mg (0.26 mmol, 53%) colorless solid

HPLC (C4): $t_R = 10.18 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.88-7.86 (m, 2H, ar.H), 7.58-7.56 (m, 2H, ar.H), 4.54 (t, *J* = 6.2 Hz, 1H, -NH-), 4.04 (t, *J* = 6.8 Hz, 2H, -CH₂OOC), 2.95 (dt, *J* = 6.7 Hz, 6.6 Hz, 2H, -C<u>H₂NHCO</u>), 2.26 (t, *J* = 7.3 Hz, 2H, -CH₂COO), 2.18 (dt, *J* = 2.7 Hz, 7.1 Hz, 2H, -C<u>H₂CCH</u>), 1.94 (t, *J* = 2.6 Hz, 1H,-CCH), 1.60-1.47 (m, 8H, alk.H), 1.42-1.37 (m, 2H, alk.H), 1.34-1.29 (m, 10H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.6$ (-COO), 139.7(-C_{ar}-SO₂), 138.3 (2 ar.C), 128.5 (2 arom.C), 99.89 (-C_{ar}-I), 84.74 (-<u>C</u>CH), 68.09 (-C<u>C</u>H), 64.56 (-CH₂OOC), 42.94 (-CH₂NHSO₂), 33.92 (-CH₂COO), 29.32 (alk.C), 29.22 (alk.C), 29.14 (alk.C), 28.97 (alk.C), 28.67 (alk.C), 28.58 (alk.C), 28.43 (alk.C), 25.89 (alk.C), 25.86 (alk.C), 24.14 (alk.C), 18.37 (alk.C)

2-lodobenzoylamido-benzoic acid undec-10-inyl-ester (90)

The synthesis proceeded according to **GP14** with 225.7 mg (0.79 mmol) 2-aminobenzoic acid undec-10-inyl-ester (**88**), 215.9 mg (0.79 mmol) 2-iodebenzoylchloride, 83.0 mg (0.82 mmol) triethylamine and 1.5 ml DCM. The crude product was purified via flash chromatography (silica, CH:EA 3:1).

 $R_f = 0.44$ (CH:EA 3:1)

Yield: 340.2 mg (0.66 mmol, 84%) yellowish oil

HPLC (C4): $t_R = 10.25 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): $\delta = 11.43$ (br s, 1H, -NH-), 8.89 (d, J = 8.0 Hz, 1H, ar.H), 8.08 (dd, J = 8.0 Hz, 1.6 Hz, 1H, ar.H), 7.94 (dd, J = 8.0 Hz, 1.0 Hz, 1H, ar.H), 7.62 (ddd, J = 8.6 Hz, 7.3 Hz, 1.4 Hz, 1H, ar.H), 7.56 (dd, J = 7.6 Hz, 1.6 Hz, 1H, ar.H), 7.44 (dt, J = 7.5Hz, 1.1Hz, 1H, ar.H), 7.15 (dddd, J = 7.8, Hz, 7.6 Hz, 5.9 Hz, 1.3 Hz, 2H, ar.H), 4.28 (t, J = 6.6 Hz, 2H, -CH₂OOC-), 2.17 (dt, J = 7.1 Hz, 2.6 Hz, 2H, -CH₂CCH), 1.93 (t, J = 2.6 Hz, 1H, -CCH), 1.75 (tt, J = 7.3Hz, 6.9 Hz, 2H, alk.H), 1.51 (tt, J = 7.6 Hz, 7.0 Hz, 2H, alk.H), 1.41-1.37 (m, 4H, alk.H), 1.35-1.30 (m, 6H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 168.2$ (-COO), 167.6 (-CONH), 142.0 (-<u>C</u>_{ar}CONH-), 141.2 (-<u>C</u>_{arom}NHCO), 140.4 (ar.C), 134.6 (ar.C), 131.4 (ar.C), 130.8 (ar.C), 128.3 (ar.C), 128.0 (ar.C), 123.0 (ar.C), 120.6 (ar.C), 115.7 (-<u>C</u>_{ar}COO), 92.69 (-C_{ar}-I), 84.65 (-<u>C</u>CH), 68.09 (-C<u>C</u>H), 65.59 (-<u>C</u>H₂OOC), 29.10 (alk.C), 28.94 (alk.C), 28.63 (alk.C), 28.62 (alk.C), 28.45 (alk.C), 28.68 (alk.C), 25.92 (alk.C), 18.33 (alk.C)

4-lodobenzoylamido-benzoesäure-undec-10-inyl-ester (92)

The synthesis proceeded according to **GP14** with 200.0 mg (0.70 mmol) 2-aminobenzoic acid undec-10-inyl-ester (**88**), 189.2 mg (0.70 mmol) 4-iodobenzoylchloride, 73.9 mg (0.73 mmol) triethylamine and 1.2 ml DCM. The crude product was purified via flash chromatography (silica, CH:EA 3:1).

 $R_f = 0.42$ (CH:EA 3:1)

Yield: 208.2 mg (0.40 mmol, 58%) colorless oil

HPLC (C4): $t_R = 10.35 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 12.11 (br s, 1H, -NH-), 8.89 (d, *J* = 8.6 Hz, 1H, ar.H), 8.08 (d, *J* = 8.0 Hz, 1H, ar.H), 7.88-7.86 (m, 2H, ar.H), 7.77-7.75 (m, 2H, ar.H), 7.62-7.58 (m, 1H, ar.H), 7.16-7.12 (m, 1H, ar.H), 4.35 (t, *J* = 6.6 Hz, 2H, -CH₂OOC-), 2.20-2.16 (m, 2H, -C<u>H₂</u>CCH), 1.94 (t, *J* = 2.6 Hz, 1H, -CCH), 1.81-1.76 (m, 2H, alk.H), 1.54-1.49 (m, 2H, alk.H), 1.45-1.33 (m, 10H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 168.7$ (-COO), 164.9 (-CONH), 141.6 (-<u>Car</u>NHCO), 138.0 (2 ar.C), 134.7 (ar.C), 134.4 (ar.C), 130.9 (2 ar.C), 128.9 (ar.C), 122.8 (ar.C), 120.4 (ar.C), 115.4 (-<u>Car</u>COO), 99.15 (-C_{arom}-I), 84.69 (-<u>C</u>CH), 68.10 (-C<u>C</u>H), 65.72 (-<u>C</u>H₂OOC), 29.32 (alk.C), 29.15 (alk.C), 28.98 (alk.C), 28.66 (alk.C), 28.52 (alk.C), 28.42 (alk.C), 25.97 (alk.C), 18.37 (alk.C)

10-Oxa-3-aza-bicyclo[20.2.2]hexacosa-1(25),22(26),23-trien-20-in-2,9-dione (25)

The synthesis proceeded according to **GP17** with 40.0 mg (0.078 mmol) 6-(4-iodebenzamido)hexanoic acid undec-10-inyl-ester (**82**), 15.0 mg (0.0078 mmol) Pd-resin **1a/Pd** or 9.0 mg (0.0078 mmol) Pd[PPh₃]₄, 1.5 mg (0.0078 mmol) CuI in 1.95 ml dioxane:piperidine (2:1). The crude product was purified via flash chromatography (silica, CH:EA 1:1).

 $R_{\rm f} = 0.54$ (CH:EA 1:1)

Yield: 3.9 mg (beads) (0.0101 mmol, 13%) yellowish oil

2.6 mg (homogenous) (0.00678 mmol, 9%) yellowish oil

HPLC (C4): $t_R = 8.68 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.82 (d, *J* = 8.6 Hz, 2H, ar.H), 7.41 (d, *J* = 8.6 Hz, 2H, ar.H), 6.99 (br s, 1H, -NH-), 4.00-3.96 (m, 2H, -CH₂OOC-), 3.60 (dt, *J* = 5.9 Hz, 11.7 Hz, 2H, -CH₂NHCO-),

2.46-2.43 (m, 2H, -C<u>H</u>₂COO), 2.37-2.32 (m, 2H, -C<u>H</u>₂CCH), 1.67-1.56 (m, 6H, alk.H), 1.50-1.45 (m, 2H, alk.H), 1.43-1.35 (m, 6H, alk.H), 1.31-1.25 (m, 6H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 174.6$ (-COO), 166.9 (-CONH), 137.7 (ar.C), 133.6 (-<u>C</u>_{arom}CONH-), 131.2 (ar.C), 128.5 (ar.C), 127.1 (2 ar.C), 93.46 (-<u>C</u>CH), 81.30 (-C<u>C</u>H), 65.19 (-<u>C</u>H₂OOC), 37.24 (-<u>C</u>H₂NHCO), 33.10 (-<u>C</u>H₂COO), 29.18 (alk.C), 28.98 (alk.C), 28.64 (alk.C), 27.86 (alk.C), 27.24 (alk.C), 27.07 (alk.C), 26.81 (alk.C), 25.92 (alk.C), 24.63 (alk.C), 21.40 (alk.C), 19.10 (alk.C)

HRMS (FAB, 3-NBA) for $C_{24}H_{34}NO_3 [M+H]^+$:	calcd.:	384.2539
	found:	384.2529
for C ₂₄ H ₃₃ NO ₃ Na [M+Na] ⁺ :	calcd.:	406.2358
	found:	406.2367

Benzo-2-aza-9-oxacyclodocosan-19-in-1,8-dione (23)

The synthesis proceeded according to **GP17** with 40.0 mg (0.078 mmol) 6-(2-iodobenzamido)hexanoic acid undec-10-inyl-ester (**80**), 15.0 mg (0.0078 mmol) Pd-resin **1a/Pd** or 9.0 mg (0.0078 mmol) Pd[PPh₃]₄, 1.5 mg (0.0078 mmol) CuI in 1.95 ml dioxane:piperidine (2:1). The crude product was purified via flash chromatography (silica, CH:EA 1:1).

 $R_f = 0.52$ (CH:EA 1:1)

Yield: 8.0 mg (beads) (0.0209 mmol, 27%) yellowish oil

8.7 mg (homogeneous) (0.0227 mmol, 29%) yellowish oil

HPLC (C4): $t_R = 8.54 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 8.06-8.04 (m, ar.H), 7.60 (br s, 1H, -NH-), 7.38-7.36 (m, 2H, arom.H), 4.14 (t, *J* = 5.7Hz, 2H, -CH₂OOC-), 3.45 (dt, *J* = 9.8 Hz, 5.7 Hz, 2H, -CH₂NHCO), 2.46 (t, *J* = 7.6 Hz, 2H, -CH₂COO-), 2.35 (dt, *J* = 2.4 Hz, 7.3 Hz, 2H, -CH₂CCH), 1.73-1.63 (m, 10H, alk.H), 1.48-1.25 (m, 10H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.4$ (-COO), 166.2 (-CONH-), 135.2 (ar.H), 133.5 (ar.H), 130.3 (ar.H), 130.0 (ar.H), 128.2 (ar.H), 120.0 (ar.C), 97.26 (-<u>C</u>C-C_{ar}), 79.46 (-C<u>C</u>-C_{ar}), 63.77 (-<u>C</u>H₂OOC), 40.05 (-<u>C</u>H₂NHCO), 34.96 (-<u>C</u>H₂COO), 29.76 (alk.C), 28.84 (alk.C), 28.79 (alk.C), 28.50 (alk.C), 28.13 (alk.C), 28.07 (alk.C), 27.93 (alk.C), 26.75 (alk.C), 25.53 (alk.C), 25.10 (alk.C), 19.62 (alk.C)

HRMS (FAB, 3-NBA) for $C_{24}H_{34}NO_3 [M+H]^+$:	calcd.:	384.2539
	found:	384.2574

2,2-Dioxo-10-oxa-2λ6-thia-3-aza-bicyclo[15.2.2]heneicosa-1(20),17(21),18-trien-15-in-9one (26)

The synthesis proceeded according to **GP17** with 30.0 mg (0.063 mmol) 6-(4-iodobenzenesulfonyl)hexanoic acid hex-5-inyl-ester (**85**), 12.1 mg (0.0063 mmol) Pd-resin **1a/Pd** or 7.3 mg (0.0063 mmol) $Pd[PPh_3]_4$, 1.2 mg (0.0063 mmol) CuI in 1.57 ml dioxane:piperidine (2:1). The crude product was purified via flash chromatography (silica, CH:EA 1:1).

 $R_{\rm f} = 0.32$

Yield: 2.6 mg (beads) (0.0074 mmol, 12%) yellowish oil

1.4 mg (homogeneous) (0.0040 mmol, 6%) yellowish oil

HPLC (C4): $t_R = 6.80 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.83-7.81 (m, 2H, ar.H), 7.51-7.48 (m, 2H, ar.H), 4.19 (t, *J* = 5.4 Hz, 2H, -CH₂OOC-), 3.08 (dt, *J* = 6.0 Hz, 5.7 Hz, 2H, -C<u>H₂NHCO-</u>), 2.44 (t, *J* = 5.4 Hz, 2H, -CH₂COO), 2.23 (dt, *J* = 2.7 Hz, 6.9 Hz, 2H, -C<u>H₂CCH</u>), 1.84-1.79 (m, 10H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.3$ (-COO), 138.9 (-C_{ar}-SO₂), 132.0 (2 ar.C), 128.7 (2 ar.C), 127.2 (ar.C), 95.37 (-<u>C</u>C-C_{ar}), 80.12 (-C<u>C</u>-C_{ar}), 63.12 (-<u>C</u>H₂OOC), 41.89 (-CH₂NHSO₂), 33.25 (-CH₂COO), 28.81 (alk.C), 27.89 (alk.C), 26.91 (alk.C), 24.76 (alk.C), 23.42 (alk.C), 18.97 (alk.C)

HRMS (FAB, 3-NBA) for $C_{18}H_{24}NO_4S$ [M+H] ⁺ :	calcd.:	350.1426
	found:	350.1425

8,9,10,11,12,13,14,15-Octahydro-7*H*,23*H*-6-oxa-23-aza-dibenzocyclononadecen-16-in-5,22-dione (29)

The synthesis proceeded according to **GP17** with 40.0 mg (0.077 mmol) 2-iodobenzoylamido-benzoic acid undec-10-inyl-ester (**90**), 14.8 mg (0.0077 mmol) Pd-resin **1a/Pd** or 8.9 mg (0.0077 mmol) Pd[PPh₃]₄, 1.7 mg (0.0077 mmol) CuI in 2.20 ml dioxane:piperidine (2:1). The crude product was purified via prep. HPLC.

Yield: 9.8 mg (beads) (0.0251 mmol, 33%) yellowish oil

10.5 mg (homogeneous) (0.0269 mmol, 35%) yellowish oil

HPLC (C4): $t_R = 9.65 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 11.61 (br s, 1H, -NH-), 8.85 (dd, *J* = 8.4 Hz, 1.1 Hz, 1H, ar.H), 8.11 (dd, *J* = 7.9 Hz, 1.7 Hz, 1H, ar.H), 7.68 (dd, *J* = 7.0 Hz, 2.2 Hz, 1H, ar.H), 7.61 (ddd, *J* = 8.5 Hz, 7.3 Hz, 1.4 Hz, 1H, ar.H), 7.50 (dd, *J* = 6.8 Hz, 1.7 Hz, 1H, ar.H), 7.37 (quind, *J* = 7.5Hz, 1.7 Hz, 2H, ar.H), 7.14 (ddd, *J* = 8.1, Hz, 7.3 Hz, 1.1 Hz, 2H, ar.H), 4.41 (t, *J* = 5.7 Hz, 2H, -CH₂OOC-), 2.28 (t, *J* = 7.1 Hz, 2H, -C<u>H₂CCH</u>), 1.81 (tt, *J* = 6.2Hz, 6.0 Hz, 2H, alk.H), 1.48 (tt, *J* = 7.0 Hz, 6.7 Hz, 2H, alk.H), 1.40-1.32 (m, 4H, alk.H), 1.31-1.24 (m, 6H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 167.7$ (-COO), 167.3 (-CONH), 141.4 (-<u>C</u>_{ar}CONH-), 139.1 (-<u>C</u>_{ar}NHCO), 134.5 (ar.C), 133.1 (ar.C), 130.8 (ar.C), 130.1 (ar.C), 128.6 (ar.C), 127.8 (ar.C), 122.8 (ar.C), 121.0 (ar.C), 115.7 (-<u>C</u>_{ar}COO), 96.26 (-<u>C</u>C-C_{ar}), 77.95 (-C<u>C</u>-C_{ar}), 64.51 (-<u>C</u>H₂OOC), 28.11 (alk.C), 27.95 (alk.C), 27.50 (alk.C), 27.36 (alk.C), 26.91 (alk.C), 26.56 (alk.C), 23.60 (alk.C), 18.33 (alk.C)

HRMS (FAB, 3-NBA) for $C_{25}H_{28}NO_3 [M+H]^+$: calcd.: 390.2069 found: 390.2084

11-Oxa-3-aza-tricyclo[21.2.2.0^{4,9}]heptacosa-1(26),4,6,8,23(27),24-hexaen-21-in-2,10dione (30)

The synthesis proceeded according to **GP17** with 30.0 mg (0.058 mmol) 4-iodbenzoylamido-benzooic acid undec-10-inyl-ester (**92**), 11.2 mg (0.0058 mmol) Pd-resin **1a/Pd** or 6.7 mg (0.0058 mmol) Pd[PPh₃]₄, 1.1 mg (0.0058 mmol) CuI in 1.45 dioxane:piperidine (2:1). The crude product was purified via prep. HPLC.

Yield: 3.2 mg (beads) (0.0082 mmol, 14%) yellowish oil

3.2 mg (homogeneous) (0.0082 mmol, 14%) yellowish oil

HPLC (C4): $t_R = 8.87 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): $\delta = 10.15$ (br s, 1H, -NH-), 8.60 (dd, J = 8.4 Hz, 1.0 Hz, 1H, ar.H), 8.13 (dd, J = 8.1 Hz, 1.5 Hz, 1H, ar.H), 7.72-7.70 (m, 2H, ar.H), 7.60 (ddd, J = 8.4 Hz, 7.1 Hz, 1.5 Hz, 1H, ar.H), 7.52-7.50 (m, 2H, ar.H), 7.19 (ddd, J = 8.0 Hz, 7.3 Hz, 0.9 Hz, 1H, ar.H), 4.25 (t, J = 8.5 Hz, 2H, -CH₂OOC-), 2.47 (t, J = 6.2 Hz, 2H, -CH₂CCH), 1.90-1.85 (m, 2H, alk.H), 1.62-1.60 (m, 4H, alk.H), 1.48-1.35 (m, 8H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): δ = 167.1 (-COO), 165.7 (-CONH), 139.0 (-<u>C</u>_{ar}CONH-), 135.6 (-<u>C</u>_{ar}NHCO), 134.6 (ar.C), 134.3 (ar.C), 132.8 (ar.C), 131.9 (ar.C), 127.9 (ar.C), 127.0 (ar.C), 126.9 (ar.C), 123.7 (ar.C), 121.0 (ar.C), 117.9 (-<u>C</u>_{ar}COO), 95.11 (-<u>C</u>C-C_{ar}), 77.20 (-C<u>C</u>-C_{ar}), 66.49 (-<u>C</u>H₂OOC), 30.08 (alk.C), 29.99 (alk.C), 28.25 (alk.C), 27.79 (alk.C), 26.91 (alk.C), 26.26 (alk.C), 25.78 (alk.C), 18.72 (alk.C) HRMS (FAB, 3-NBA) for $C_{25}H_{27}NO_3 [M]^+$:

calcd.: 389.1991 found: 389.1994

3,16-Dioxa-bicyclo[21.2.2]heptacosa-1(26),23(27),24-trien-21-in-2,15-dione (21)

The synthesis proceeded according to **GP17** with 50.1 mg (0.095 mmol) 12-(4-iodobenzoyl)dodecanoic acid hex-5-inyl-ester (**73**), 18.3 mg (0.0095 mmol) Pd-resin **1a/Pd**, 1.8 mg (0.0095 mmol) CuI in 2.40 ml dioxane:piperidine (2:1). The crude product was purified via prep. HPLC.

Yield: 9.6 mg (beads) (0.024 mmol, 25%) yellowish oil

HPLC (C4): $t_R = 9.16 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.90 (d, 8.6 Hz, 2H, ar.H), 7.37 (d, 8.4 Hz, 2H, ar.H), 4.30 (t, *J* = 5.3 Hz, 2H, -CH₂OOC-Ar), 4.13 (t, *J* = 6.1 Hz, 2H, CH₂OOC-), 2.44 (t, *J* = 6.1 Hz, 2H, -CH₂COO), 2.23 (t, *J* = 7.5 Hz, 2H, C<u>H₂CC-C_{ar}), 1.87-1.80 (m, 2H, alk.H), 1.74-1.62 (m, 4H, alk.H), 1.57-1.49 (m, 2H, alk.H), 1.48-1.47 (m, 2H, alk.H), 1.36-1.32 (m, 2H, alk.H), 1.28-1.22 (m, 4H, alk.H), 1.19-1.15 (m, 6H, alk.H)</u>

¹³C-NMR (100 MHz, CDCl₃): $\delta = 174.1$ (-COO), 166.2 (Ar-COO), 131.2 (2 ar.C), 129.3 (ar.C), 129.2 (2 ar.C), 128.6 (ar.C), 93.35 (-<u>C</u>C-C_{ar}), 81.01 (-C<u>C</u>-C_{ar}), 65.47 (-<u>C</u>H₂OOC-Ar), 63.73 (-<u>C</u>H₂OOC), 34.41 (-CH₂COO), 30.04 (alk.C), 29.15 (alk.C), 29.04 (alk.C), 28.46 (alk.C), 27.95 (alk.C), 27.56 (alk.C), 27.23 (alk.C), 26.78 (alk.C), 25.84 (alk.C), 25.34 (alk.C), 24.75 (alk.C), 18.92 (alk.C)

HRMS (FAB, 3-NBA) for $C_{25}H_{34}O_4 [M]^+$:	calcd.:	398.2457
	found:	398.2452

8,9,10,11,12,13,14,15,16,17,20,21,22,23-Tetradecahydro-7*H*-6,19-dioxabenzocyclotricosene-24-in-5,18-dione (20)

The synthesis proceeded according to **GP17** with 50.7 mg (0.095 mmol) 12-(2-iodobenzoyl)dodecanoic acid hex-5-inyl-ester (**19**), 18.3 mg (0.0095 mmol) Pd-resin **1a/Pd** or 22.0 mg (0.019 mmol) Pd[PPh₃]₄, 3.6 mg (0.019 mmol) CuI in 2.20 ml dioxane:piperidine (2:1). The crude product was purified via prep. HPLC.

Yield: 8.3 mg (beads) (0.021 mmol, 22%) yellowish oil

8.3 mg (homogeneous) (0.021 mmol, 22%) yellowish oil

HPLC (C4): 8.85 min

¹H-NMR (400 MHz, CDCl₃): $\delta = 7.87$ (d, J = 7.8 Hz, 1H, ar.H), 7.50 (d, J = 7.8 Hz, 1H, ar.H), 7.41 (dt, J = 7.5 Hz, 1.4 Hz, 1H, ar.H), 7.32 (dt, J = 7.6 Hz, 0.9 Hz, 1H, ar.H), 4.353 (t, J = 6.5 Hz, 2H, - CH₂OOC-Ar), 4.15 (t, J = 6.1, 2H, CH₂OOC-), 2.51 (t, J = 6.7 Hz, 2H, -CH₂COO), 2.32 (t, J = 6.9 Hz, 2H, - CH₂CCH), 1.86-1.70 (m, 6H, alk.H), 1.69-1.62 (m, 2H, alk.H), 1.51-1.43 (m, 2H, alk.H), 1.35-1.26 (m, 12H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.8$ (-COO), 166.9 (Ar-COO), 134.0 (ar.C), 132.6 (ar.C), 131.1 (ar.C), 130.1 (ar.C), 127.2 (ar.C), 123.6 (ar.C), 94.44 (-<u>C</u>C-C_{ar}), 79.80 (-C<u>C</u>-C_{ar}), 65.40 (-<u>C</u>H₂OOC-Ar), 63.88 (-<u>C</u>H₂OOC), 34.47 (-CH₂COO), 28.85 (alk.C), 28.76 (alk.C), 28.60 (alk.C), 28.32 (alk.C), 28.29 (alk.C), 28.24 (alk.C), 28.23 (alk.C), 27.84 (alk.C), 25.88 (alk.C), 25.61 (alk.C), 24.76 (alk.C), 19.81 (alk.C)

HRMS (FAB, 3-NBA) for $C_{25}H_{35}O_4$ [M+H]⁺: calcd.: 399.2535 found: 399.2527

for $C_{25}H_{34}O_4Na [M+Na]^+$: calcd.: 421.2355 found: 421.2332

10-Oxa-3-aza-bicyclo[15.2.2]heneicosa-1(20),17(21),18-trien-15-in-2,9-dione (22)

The synthesis proceeded according to **GP17** with 40.0 mg (0.091 mmol) 6-(4-iodobenzamido)hexanoic acid hex-5-inyl-ester (**79**), 17.5 mg (0.0091 mmol) Pd-resin **1a/Pd** or 10.5 mg (0.0091 mmol) Pd[PPh₃]₄, 1.7 mg (0.0091 mmol) CuI in 2.27 ml dioxane:piperidine (2:1). The crude product was purified via prep. HPLC.

Yield: 14.2 mg (beads) (0.0453 mmol, 50%) yellowish oil

11.4 mg (homogeneous) (0.0364 mmol, 40%) yellowish oil

HPLC (C4): $t_R = 6.52 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 8.09-8.07 (m, 1H, ar.H), 7.64 (br s, 1H, -NH-), 7.46-7.44 (m, 1H, ar.H), 7.38-7.36 (m, 2H ar.H), 4.23 (t, *J* = 5.6 Hz, 2H, -CH₂OOC-), 3.50 (t, *J* = 6.0 Hz, 2H, -CH₂NHCO), 2.56 (t, *J* = 7.1 Hz, 2H, -CH₂COO), 2.40-2.37 (m, 2H, -CH₂-CCH), 1.84-1.71 (m, 6H, alk.H), 1.68-1.61 (m, 2H, alk.H), 1.52-1.46 (m, 2H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.6$ (-COO), 166.1 (-CONH), 134.8 (ar.C), 133.8 (ar.C), 130.3 (ar.C), 130.1 (ar.C), 128.2 (ar.C), 119.9 (ar.C), 96.59 (-<u>C</u>C-C_{ar}), 79.93 (-C<u>C</u>-C_{ar}), 63.11 (-<u>C</u>H₂OOC), 40.44 (-<u>C</u>H₂NHCO), 34.36 (-<u>C</u>H₂COO), 28.89 (alk.C), 27.90 (alk.C), 27.14 (alk.C), 25.55 (alk.C), 24.16 (alk.C), 19.30 (alk.C)

HRMS (FAB, 3-NBA) for $C_{19}H_{24}NO_3 [M+H]^+$: calcd.: 314.1756 found: 314.1770

2,2-Dioxo-10-oxa-2λ6-thia-3-aza-bicyclo[20.2.2]hexacosa-1(25),22(26),23-trien-20-in-9one (26)

The synthesis proceeded according to **GP17** with 30.0 mg (0.055 mmol) 6-(4-iodobenzenesulfonyl)hexanoic acid undec-10-inyl-ester (**85**), 10.5 mg (0.0055 mmol) Pd-resin **1a/Pd** or 6.3 mg (0.0055 mmol) Pd[PPh₃]₄, 1.0 mg (0.0055 mmol) CuI in 1.37 ml dioxane:piperidine (2:1). The crude product was purified via prep. HPLC.

Yield: 2.6 mg (beads) (0.0074 mmol, 12%) yellowish oil

1.4 mg (homogeneous) (0.0040 mmol, 6%) yellowish oil

HPLC (C4): $t_R = 8.49 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.80-7.78 (m, 2H, ar.H), 7.51-7.49 (m, 2H, ar.H), 4.39 (t, *J* = 6.2 Hz, 1H, -NH-), 4.03 (t, *J* = 6.9 Hz, 2H, -CH₂OOC-), 2.98 (dt, *J* = 7.0 Hz, 6.2 Hz, 2H, -C<u>H₂NHCO-</u>), 2.47 (t, *J* = 6.3 Hz, 2H, -CH₂COO), 2.17 (t, *J* = 7.1 Hz, 2H, -C<u>H₂CCH</u>), 1.59-1.54 (m, 4H, alk.H), 1.46-1.40 (m, 4H, alk.H), 1.38-1.33 (m, 2H, alk.H)

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.4$ (-COO), 138.4 (-C_{ar}-SO₂), 131.9 (2 ar.C), 127.1 (2 ar.C), 124.8 (ar.C), 94.66 (-<u>C</u>C-C_{ar}), 80.17 (-C<u>C</u>-C_{ar}), 64.38 (-<u>C</u>H₂OOC), 42.87 (-CH₂NHSO₂), 33.92 (-CH₂COO), 28.58 (alk.C), 28.50 (alk.C), 28.32 (alk.C), 28.05 (alk.C), 27.74 (alk.C), 27.32 (alk.C), 27.21 (alk.C), 25.68 (alk.C), 25.40 (alk.C), 24.07 (alk.C), 19.08 (alk.C)

HRMS (FAB, 3-NBA) for $C_{18}H_{24}NO_4S [M+H]^+$:	calcd.:	350.1426
	found:	350.1425

Experiments related to Suzuki-reactions

General procedure for the silulation of $1,\omega$ -alkinols (GP18)

In an oven dried flask a solution of 1.1 eq TBDMSCl, 1.2 eq triethylamine and 0.05 eq DMAP in abs. DCM is prepared. Then a solution of 1 eq 1, ω -alkinol in DCM is added at 0°C. The reaction mixture is stirred for 2 h at 0°C and 24 h at RT, and then washed with satd. NH₄Cl-solution. The aqueous layer is extracted with Et₂O (3x). The combined organic layers are washed with 1x NaHCO₃-solution and 1x

brine, dried over Na_2SO_4 . The solvents are removed in vaccuo using a rotovap. The crude product is purified via flash chromatography.

General procedure for hydroboration of 1-alkynes (GP19)

In an oven dried flask 1 eq 1-alkyne and 1.5 eq catecholborane are dissolved in abs. THF and heated to 75°C for 6 h. After cooling to RT, water is added dropwise until no gas evolution is observed. After stirring for 30 min 1 eq formaldehyde in aqueous solution are added. The reaction mixture is stirred for 1 h, then 1.1 eq. pinacol are added and the reaction mixture heavily stirred overnight. The solvents are removed in vaccuo using a rotovap. The crude product is purified via flash chromatography.

General procedure for intramolecular Suzuki-reactions (GP20)

Under inert conditions a flask is charged with Pd-beads or $Pd[PPh_3]_4$ (0.1 eq Pd). After 3 vacuum/argon cyles the beads are swollen in a degassed solution of DME:H₂O:DMF (1.5:1.5:1). After addition of 2 eq Cs₂CO₃ the reaction mixture is heated to 80°C. The substrate is added as solution in DME (2v in respect to 1v DMF of the catalyst solution). The reaction mixture is heated to 80°C over night. After comple conversion (15 h, monitored by HPLC) the reaction mixture is cooled to RT.

In reactions with Pd-beads the beads are filtered off, washed with DCM (1x45 ml, 10 min), DCM:MeOH (1:1) (2x20 ml, 2x10 min) and DCM (1x20 ml, 10 min).

The combined filtrates or the reaction mixture in the case of catalysis with $Pd[PPh_3]_4$ are washed with H_2O (1x20 ml). The aqueous phase is extracted back with DCM (3x30 ml). The combined organic layer are dried over Na_2SO_4 . The solvents are removed in vaccuo using a rotovap. The crude product is purified via flash chromatography.



1-tert-Butyldimethylsilanyloxyhex-5-ine (31)

The synthesis was performed according to **GP18** with 0.15 g (0.99 mmol) TBDMSCl, 5.5 mg (0.0045 mmol) DMAP, 0.11 g (1.08 mmol) triethylamine and 0.09 g (0.90 mmol) 1-hexinol. The crude product was purified via flash chromatography (silica, pentane).

 $R_f = 0.19$ (pentane)

Yield: 0.19 g (0.90 mmol, quant.) colorless oil

¹H-NMR (400 MHz, CDCl₃): δ = 3.63 (t, *J* = 6.1 Hz, 2H,-CH₂OSi-), 2.21 (dt, *J* = 6.9 Hz, 2.7 Hz, 2H, - C<u>H₂</u>CCH), 1.93 (t, *J* = 2.6 Hz, 1H, -CCH), 1.62-1.59 (m, 4H, alk. H), 0.89 (s, 9H, -C(CH₃)₃), 0.04 (s, 6H, -Si(CH₃)₂-).

The analytical data are in accordance to literature.^{ix}

1-tert-Butyldimethylsilanyloxyundec-10-ine (100)

The synthesis was performed according to **GP18** with 2.7 g (17.8 mmol) TBDMSCl, 98.9 mg (0.81 mmol) DMAP, 1.94 g (19.4 mmol) triethylamine and 2.72 g (16.2 mmol) 1-undecinol. The crude product was purified via flash chromatography (silica, pentane).

 $R_f = 0.15$ (pentane)

Yield: 3.81 g (13.5 mmol, 83%) colorless oil

¹H-NMR (400 MHz, CDCl₃): δ = 3.65 (t, *J* = 6.1 Hz, 2H,-CH₂OSi-), 2.22 (dt, *J* = 6.8 Hz, 2.7 Hz, 2H, - CH₂CCH), 1.91 (t, *J* = 2.6 Hz, 1H, -CCH), 1.62-1.46 (m, 16H, alk. H), 0.90 (s, 9H, -C(CH₃)₃), 0.05 (s, 6H, -Si(CH₃)₂-).

(*E*)-1-tert-Butyldimethylsilanyloxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5ene (93)

The synthesis was performed according to **GP19** with 0.66 g (3.14 mmol) 1-*tert*butyldimethylsilanyloxyhex-5-ine (**31**), 4.7 ml (4.7 mmol) 1M-catecholborane solution in abs. THF, 3 ml H₂O, 2.6 ml (3.14 mmol) formaldehyde-solution and 0.41 g (3.45 mmol) pinacol. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:1).

 $R_f = 0.67$ (cyclohexane:ethylacetate 3:1)

Yield: 0.18 g (0.52 mmol, 17%) colorless oil

¹H-NMR (400 MHz, CDCl₃): $\delta = 6.61$ (dt, J = 18.0 Hz, 6.5 Hz, 1H, CH=CH), 5.45-4.41 (m, 1H, CH=CH), 3.58 (t, J = 6.1 Hz, 2H,-CH₂OSi-), 2.15 (m, 2H, -C<u>H</u>₂CH=CH), 1.53-1.43 (m, 4H, alk. H), 1.24 (s, 12H, -CH₃), 0.87 (s, 9H, -C(CH₃)₃), 0.02 (s, 6H, -Si(CH₃)₂-).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 154.5$ (-<u>C</u>H=CH-B), 118.4 (-CH=<u>C</u>H-B), 82.98 (-<u>C</u>(CH₃)₂), 62.98 (-<u>C</u>H₂O), 35.54 (alk.C), 32.22 (alk.C), 25.98 (alk.C), 25.97 (-CH₃), 25.96 (-CH₃), 25.95 (-CH₃), 25.94 (-CH₃), 24.76 (-CH₃), 24.57 (-CH₃), 24.47 (-CH₃), 18.35 (<u>C</u>(CH₃)₃), -5.29 (-Si(CH₃)₂)

(*E*)-1-tert-Butyldimethylsilanyloxy-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)undec-10-ene (101)

The synthesis was performed according to **GP19** with 2.0 g (7.1 mmol) 1-*tert*butyldimethylsilanyloxyundec-10-ine (**100**), 10.6 ml (10.6 mmol) 1M-catecholborane-solution in abs. THF, 16 ml H₂O, 5.8 ml (7.1 mmol) formaldehyde-solution and 0.92 g (7.8 mmol) pinacol. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:1).

 $R_f = 0.65$ (cyclohexane:ethylacetate 3:1)

Yield: 1.96 g (4.78 mmol, 67%) yellowish oil

¹H-NMR (400 MHz, CDCl₃): $\delta = 6.87-6.76$ (m, 1H, CH=CH), 5.70-5.58 (m, 1H, CH=CH), 3.65-3.61 (m, 2H,-CH₂OSi-), 2.43-2.39 (m, 2H, -C<u>H₂CH=CH)</u>, 1.53-1.43 (m, 4H, alk. H), 1.24 (s, 12H, -CH₃), 0.88 (s, 9H, -C(CH₃)₃), 0.04 (s, 6H, -Si(CH₃)₂-).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 154.8$ (-<u>C</u>H=CH-B), 118.5 (-CH=<u>C</u>H-B), 82.97 (-<u>C</u>(CH₃)₂), 63.32 (-<u>C</u>H₂O), 35.81 (alk.C), 32.87 (alk.C), 29.53 (alk.C), 29.42 (alk.C), 29.21 (alk.C), 28.21 (alk.C), 25.98 (alk.C), 25.78 (-CH₃), 24.76 (-CH₃), 24.56 (-CH₃), 18.37 (<u>C</u>(CH₃)₃), -5.26 (-Si(CH₃)₂)

(E)-6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-ol (32)

The synthesis was performed according to **GP19** with 0.66 g (3.14 mmol) 1-*tert*butyldimethylsilanyloxyhex-5-ine (**31**), 4.7 ml (4.7 mmol) 1M-catecholborane-solution in abs. THF, 3 ml H₂O, 2.6 ml (3.14 mmol) formaldehyde-solution and 0.41 g (3.45 mmol) pinacol. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:1).

 $R_f = 0.30$ (cyclohexane:ethylacetate 3:1)

Ausbeute: 0.28 g (1.23 mmol, 39%) farbloses Öl

The synthesis was performed according to **GP8** mit 37.3 mg (0.11 mmol) (*E*)-1-*tert*butyldimethylsilanyloxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-ene (**93**), 46.8 mg (1.26 mmol) NH₄F in 2.5 ml MeOH. The crude product was used withour further purification.

Yield: 15.3 mg (0.68 mmol, 61%) yellowish oil

¹H-NMR (400 MHz, CDCl₃): $\delta = 6.62$ (dt, J = 18.0 Hz, 6.5 Hz, 1H, CH=CH), 5.43 (dt, J = 18.0 Hz, 1.6 Hz, 1H, CH=CH), 3.63 (t, J = 6.4 Hz, 2H,-CH₂OSi-), 2.21-2.15 (m, 2H, -CH₂CH=CH), 1.60-1.56 (m, 2H, alk.H), 1.53-1.43 (m, 4H, alk. H), 1.26 (s, 12H, -CH₃).

(E)-11-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)undec-10-en-1-ol (99)

The synthesis was performed according to **GP19** with 1.56 g (7.4 mmol) 1-*tert*butyldimethylsilanyloxyundec-10-ine (**100**), 11.1 ml (11.1 mmol) 1M-catecholborane-solution in abs. THF, 16 ml dest. Wasser, 5.9 ml (7.4 mmol) formaldehyde-solution and 0.96 g (8.1 mmol) pinacol. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:1).

 $R_f = 0.26$ (cyclohexane:ethylacetate 3:1)

Yield: 0.16 g (0.54 mmol, 7%) colorless oil

The synthesis was performed according to **GP8** with 0.75 g (1.83 mmol) (*E*)-1-*tert*butyldimethylsilanyloxy-11-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-10-ene (**101**), 0.78 mg (21.0 mmol) NH₄F in 40 ml MeOH. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:1).

Yield: 0.62 g (2.1 mmol, 33%) yellowish oil

¹H-NMR (400 MHz, CDCl₃): $\delta = 6.63$ (dt, J = 18.0 Hz, 6.4 Hz, 1H, CH=CH), 5.42 (dt, J = 18.0 Hz, 1.6 Hz, 1H, CH=CH), 3.64 (t, J = 6.6 Hz, 2H,-CH₂OSi-), 2.17-2.11 (m, 2H, -CH₂CH=CH), 1.58-1.52 (m, 4H, alk.H), 1.42-1.37 (m, 2H, alk. H), 1.34-1.27 (m, 8H, alk. H), 1.26 (s, 12H, -CH₃).

6-(4-lodbenzamido)-hexansäure-6-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-hex-5enyl-ester (95)

The synthesis was performed according to **GP9** with 0.11 g (0.5 mmol) 6-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-hex-5-ene (**32**), 0.18 g (0.5 mmol) 6-(4-iodobenzamido)-hexanoic acid (**78**), 30.5 mg (0.25 mmol) DMAP, 69.4 mg (0.55 mmol) DIC in 5 ml DCM and 1 ml DMF. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:1).

 $R_f = 0.33$ (cyclohexane:ethylacetate 3:1)

Yield: 0.13 g (0.23 mmol, 46%) colorless oil

HPLC (C18): $t_R = 10.94 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.78-7.76 (m, 2H, ar.H), 7.50-7.48 (m, 2H, ar.H), 6.60 (dt, *J* = 18.0 Hz, 6.5 Hz, 1H, CH=CH), 6.23 (br s, 1H, -NH-), 5.44 (dt, *J* = 18.0 Hz, 1.6 Hz, 1H, CH=CH), 4.05 (t, *J* = 6.5 Hz, 2H, -CH₂OOC-), 3.44 (dt, *J* = 6.2 Hz, 6.8 Hz, 2H, -C<u>H₂NH-</u>), 2.31 (t, *J* = 7.2 Hz, 2H, -CH₂COO-), 2.21-2.15 (m, 2H, -C<u>H₂CH=CH</u>), 1.70-1.59 (m, 6H, alk.H), 1.51-1.36 (m, 4H, alk. H), 1.26 (s, 12H, -CH₃).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.7$ (-COO), 166.6 (-CONH), 153.6 (-CH=CH-B), 137.7 (ar.H), 134.1 (ar.C), 128.5 (ar.C), 98.16 (-C_{ar}I), 83.06 (-<u>C</u>(CH₃)₂), 64.22 (-<u>C</u>H₂OOC), 39.77 (-<u>C</u>H₂NHCO), 35.18 (alk.C), 34.01 (-<u>C</u>H₂-CC), 29.11 (alk.C), 28.11 (alk.C), 26.32 (alk.C), 24.84 (alk.C), 24.76 (alk.C), 24.52 (alk.C), 24.33 (alk.C)

HRMS (FAB, 3-NBA) for $C_{25}H_{37}BINO_5 [M]^+$: calcd.: 569.1809 found: 569.1898

> für $C_{25}H_{38}BINO_5 [M+H]^+$: calcd.: 570.1888 found: 570.1880

6-(2-lodobenzamido)-hexanoic acid 6-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)hex-5-enyl-ester (34)

The synthesis was performed according to **GP9** with 28.7 mg (0.13 mmol) 6-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-hex-5-ene (**32**), 45.8 mg (0.13 mmol) 6-(2-iodobenzamido)-hexanoic acid (**77**), 9.1 mg (0.07 mmol) DMAP, 20.7 mg (0.16 mmol) DIC in 1 ml DCM and 0.01 ml DMF. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:1).

 $R_f = 0.28$ (cyclohexane:ethylacetate 3:1)

Yield: 50.2 mg (0.088 mmol, 68%) colorless oil

HPLC (C18): $t_R = 10.55 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.83-7.81 (m, 1H, ar.H), 7.34-7.33 (m, 2H, ar.H), 7.08-7.03 (m, 1H, ar.H), 6.58 (dt, *J* = 17.8 Hz, 6.4 Hz, 1H, CH=CH), 5.96 (br s, 1H, -NH-), 5.44-5.39 (m, 1H, CH=CH), 4.02 (t, *J* = 6.5 Hz, 2H, -CH₂OOC-), 3.42 (dt, *J* = 7.0 Hz, 6.5 Hz, 2H, -C<u>H</u>₂NH-), 2.29 (t, *J* = 7.3 Hz, 2H, -CH₂COO-), 2.18-2.13 (m, 2H, -C<u>H</u>₂CH=CH), 1.63 (tt, *J* = 15.1 Hz, 7.5 Hz, 6H, alk.H), 1.44 (tt, *J* = 14.5 Hz, 7.2 Hz, 4H, alk. H), 1.24 (s, 12H, -CH₃).

¹³C-NMR (100 MHz, CDCl₃): δ = 173.6 (-COO), 153.7 (-<u>C</u>H=CH-B), 139.8 (ar.H), 131.0 (ar.C), 128.2 (ar.C), 118.2 (-CH=<u>C</u>H-B), 92.39 (-C_{ar}I), 83.05 (-<u>C</u>(CH₃)₂), 64.21 (-<u>C</u>H₂OOC), 39.82 (-<u>C</u>H₂NHCO), 34.11 (-<u>C</u>H₂-CC), 29.06 (alk.C), 28.12 (alk.C), 26.49 (alk.C), 24.75 (alk.C), 24.53 (alk.C), 24.51 (alk.C)

HRMS (FAB, 3-NBA) for $C_{25}H_{37}BINO_5 [M]^+$: calcd.: 569.1809 found: 569.1779

> for $C_{25}H_{38}BINO_5 [M+H]^+$: calcd.: 570.1888 found: 570.1912

6-(4-lodbenzamido)-hexansäure-11-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)undec-10-enyl-ester (96)

The synthesis was performed according to **GP9** with 0.19 g (0.33 mmol) 11-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-undec-10-ene (**99**), 0.12 g (0.33 mmol) 6-(4-iodobenzamido)-hexanoic acid (**78**), 20.2 mg (0.16 mmol) DMAP, 45.8 mg (0.36 mmol) DIC in 3 ml DCM and 0.6 ml DMF. The crude product was purified via prep. HPLC.

Yield: 84.5 mg (0.13 mmol, 40%) colorless solid

HPLC (C18): $t_R = 13.58 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.75-7.72 (m, 2H, ar.H), 7.49-7.46 (m, 2H, ar.H), 6.61 (dt, *J* = 17.9 Hz, 6.3 Hz, 1H, CH=CH), 6.40 (br s, 1H, -NH-), 5.40 (dt, *J* = 17.9 Hz, 1.5 Hz, 1H, CH=CH), 4.02 (t, *J* = 6.7 Hz, 2H, -CH₂OOC-), 3.41 (dt, *J* = 6.4 Hz, 6.8 Hz, 2H, -C<u>H₂NH-</u>), 2.29 (t, *J* = 7.3 Hz, 2H, -CH₂COO-), 2.15-2.09 (m, 2H, -C<u>H₂CH=CH</u>), 1.68-1.56 (m, 6H, alk.H), 1.42-1.35 (m, 4H, alk. H), 1.26-1.23 (br m, 22H, alk.H).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.7$ (-COO), 166.6 (-CONH), 154.7 (-CH=CH-B), 137.6 (ar.H), 134.1 (ar.C), 128.5 (ar.C), 98.12 (-C_{ar}I), 82.92 (-C(CH₃)₂), 64.48 (-CH₂OOC), 39.71 (-CH₂NHCO), 35.72 (alk.C), 33.99 (-CH₂-CC), 29.32 (alk. C), 29.30 (alk. C), 29.15 (alk.C), 29.10 (alk.C), 29.04 (alk. C), 28.55 (alk. C), 28.11 (alk.C), 26.27 (alk.C), 25.83 (alk.C), 24.71 (alk.C), 24.28 (alk.C).

HRMS (FAB, 3-NBA) for $C_{30}H_{47}BINO_5 [M]^+$: ber.: 639.2592 gef.: 639.2597

6-(2-lodobenzamido)-hexanoic acid 11-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)undec-10-enyl-ester (94) The synthesis was performed according to **GP9** with 44.3 mg (0.15 mmol) 11-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-undec-10-ene (**99**), 45.9 mg (0.15 mmol) 6-(2-iodobenzamido)-hexanoic acid (**77**), 9.1 mg (0.07 mmol) DMAP, 20.7 mg (0.16 mmol) DIC in 1 ml DCM and 0.01 ml DMF. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:1).

 $R_f = 0.26$ (cyclohexane:ethylacetate) 3:1

Yield: 26.9 mg (0.042 mmol, 28%) colorless oil

HPLC (C18): $t_R = 13.04 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): $\delta = 7.86-7.84$ (m, 1H, ar. H), 7.38-7.36 (m, 2H, ar. H), 7.11-7.00 (m, 1H, ar.H), 6.62 (dt, J = 18.1 Hz, 6.3 Hz, 1H, CH=CH), 5.81 (br s, 1H, -NH-), 5.44-5.39 (m, 1H, CH=CH), 4.04 (t, J = 7.0 Hz, 2H, -CH₂OOC-), 3.48-3.43 (m, 2H,-C<u>H</u>₂NH-), 2.32 (t, J = 7.3 Hz, 2H, -CH₂COO-), 2.17-2.10 (m, 2H, -C<u>H</u>₂CH=CH), 1.72-1.64 (m, 4H, alk. H), 1.63-1.55 (m, 4H, alk. H), 1.50-1.43 (m, 2H, alk. H), 1.42-1.36 (m, 2H, alk. H), 1.34-1.25 (br s, 20H, -CH₃).

¹³C-NMR (100 MHz, CDCl₃): δ = 173.7 (-COO), 169.3 (-CONH), 154.7 (-CH=CH-B), 142.5 (ar. C), 139.8 (ar. C), 131.0 (ar. C), 128.2 (ar. C), 128.1 (ar. C), 92.39 (-C_{ar}I), 82.97 (-<u>C</u>(CH₃)₂), 64.53 (-<u>C</u>H₂OOC), 39.83 (-<u>C</u>H₂NHCO), 35.78 (alk. C), 34.15 (-alk. C), 29.47 (alk. C), 29.39 (alk. C), 29.36 (alk.C), 29.21 (alk. C), 29.16 (alk. C), 29.08 (alk. C), 28.61 (alk. C), 28.17 (alk. C), 26.49 (alk. C), 25.91 (alk. C), 25.90 (alk. C), 24.76 (alk. C), 24.52 (alk. C), 24.23 (alk. C), 22.06 (alk. C).

HRMS (FAB, 3-NBA) for $C_{30}H_{47}BINO_5 [M]^+$: calcd.: 639.2592 found: 639.2570

6-(4-lodobenzenesulfonyl)-hexanoic acid 6-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2yl)-hex-5-enyl-ester (97)

The synthesis was performed according to **GP9** with 0.14 g (0.63 mmol) 6-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-hex-5-ene (**32**), 0.25 g (0.63 mmol) 6-(4-iodobenzenesulfonyl)-hexanoic acid (**84**), 37.9 mg (0.31 mmol) DMAP, 87.4 mg (0.69 mmol) DIC in 5 ml DCM and 0.5 ml DMF. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:1).

 $R_f = 0.31$ (cyclohexane:ethylacetate 3:1)

Yield: 0.10 g (0.17 mmol, 27%) colorless oil

HPLC (C18): $t_R = 11.23 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.88-7.85 (m, 2H, ar.H), 7.57-7.55 (m, 2H, ar.H), 6.60 (dt, *J* = 17.5 Hz, 5.7 Hz, 1H, CH=CH), 5.44-5.40 (m, 1H, CH=CH), 4.68 (t, *J* = 5.7 Hz, 1H, -NH-), 4.04 (t, *J* = 6.3 Hz, 5.7 Hz, 1H, CH=CH), 5.44-5.40 (m, 1H, CH=CH), 4.68 (t, *J* = 5.7 Hz, 1H, -NH-), 4.04 (t, *J* = 6.3 Hz, 5.7 Hz, 5

Hz, 2H, -CH₂OOC-), 2.97-2.92 (m, 2H, -C<u>H</u>₂NH-), 2.24 (t, *J* = 7.2 Hz, 2H, -CH₂COO-), 2.20-2.14 (m, 2H, -C<u>H</u>₂CH=CH), 1.70-1.45 (br m, 10H, alk.H), 1.31-1.25 (m, 12H, alk. H).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.5$ (-COO), 153.7 (-CH=CH-B), 139.8 (ar.C), 138.3 (ar.C), 128.5 (ar.C), 99.83 (-C_{ar}I), 83.09 (-<u>C</u>(CH₃)₂), 64.25 (-<u>C</u>H₂OOC), 42.94 (-<u>C</u>H₂NHSO₂), 35.15 (alk.C), 33.91 (alk.C), 29.23 (alk.C), 28.08 (alk.C), 25.90 (alk.C), 24.75 (alk.C), 24.50 (alk.C), 24.16 (alk.C).

HRMS (FAB, 3-NBA) for $C_{24}H_{38}BINO_6S [M+H]^+$:	calcd.: 606.1558
	found: 606.1599
for C ₂₄ H ₃₇ BINO ₆ SNa [M+Na] ⁺	: calcd.: 628.1377
	found: 628

6-(4-lodobenzenesulfonyl)-hexanoic acid 11-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2yl)-undec-10-enyl-ester (98)

The synthesis was performed according to **GP9** with 0.19 g (0.63 mmol) 11-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-undec-10-ene (**95**), 0.25 g (0.63 mmol) 6-(4-iodobenzenesulfonyl)-hexanoic acid (**84**), 37.9 mg (0.31 mmol) DMAP, 87.4 mg (0.69 mmol) DIC in 5 ml DCM and 0.5 ml DMF. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 3:1).

 $R_f = 0.34$ (cyclohexane:ethylacetate 3:1)

Yield: 0.15 g (0.23 mmol, 36%) colorless oil

HPLC (C18): $t_R = 10.55 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): δ = 7.85-7.83 (m, 2H, ar.H), 7.57-7.55 (m, 2H, ar.H), 6.62 (dt, *J* = 18.0 Hz, 6.4 Hz, 1H, CH=CH), 5.44-5.39 (m, 1H, CH=CH), 5.21 (t, *J* = 6.1 Hz, 1H, -NH-), 3.62 (t, *J* = 6.6 Hz, 2H, -CH₂OOC-), 2.97-2.92 (m, 2H, -C<u>H₂NH-), 2.54 (t, *J* = 7.3 Hz, 2H, -CH₂COO-), 2.16-2.10 (m, 2H, -C<u>H₂CH=CH), 1.73-1.67 (m, 2H, alk.H), 1.59-1.51 (m, 6H, alk. H), 1.49-1.35 (m, 4H, alk. H), 1.33-1. 24 (m, 20 H, alk. H).</u></u>

¹³C-NMR (100 MHz, CDCl₃): δ = 170.9 (-COO), 154.8 (-CH=CH-B), 139.6 (ar.H), 138.3 (ar. C), 128.4 (ar.C), 99.87 (-C_{ar}I), 82.97 (-C(CH₃)₂), 63.02 (-CH₂OOC), 42.84 (-CH₂NHSO₂), 36.42 (alk.C), 35.75 (alk. C), 33.76 (alk. C), 32.76 (alk. C), 32.75 (alk. C), 29.58 (alk. C), 29.52 (alk. C), 29.44 (alk. C), 29.40 (alk. C), 29.36 (alk. C), 29.34 (alk. C), 29.32 (alk. C), 29.27 (alk.C), 29.11 (alk. C), 28.14 (alk.C), 25.84 (alk.C), 25.68 (alk. C), 24.74 (alk.C), 24.21 (alk.C).

HRMS (FAB, 3-NBA) for $C_{29}H_{47}BINO_6S [M]^+$:	calcd.:	675.2262
	found:	675.2228

for $C_{29}H_{48}BINO_6S [M+H]^+$: calcd.: 676.2340 found: 676.2442

10-Oxa-3-aza-bicyclo[20.2.2]hexacosa-1(25),20,22(26),23-tetraen-2,9-dione (38)

The synthesis was performed according to **GP20** with 7.1 mg (0.0039 mmol Pd) Pd-beads **1a/Pd** or 4.5 mg (0.0039 mmol) Pd[PPh₃]₄, 25.5 mg (0.078 mmol) Cs_2CO_3 in 0.64 ml DME:H₂O:DMF (1.5:1.5:1) and 25.0 mg (0.039 mmol) 6-(4-iodobenzamido)-hexanoic acid 11-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-undec-10-enyl-ester (**96**) in 0.32 ml DME. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 1:1).

 $R_f = 0.37$ (cyclohexane:ethylacetate 1:1)

Yield: 7.1 mg (beads) (0.018 mmol, 47%) colorless solid

9.2 mg (homogeneous) (0.024, 61%) colorless solid

Schmp: nicht bestimmt

¹H-NMR (400 MHz, CDCl₃): $\delta = 7.78$ (d, J = 8.2 Hz, 2H, ar.H), 7.36 (d, J = 8.2 Hz, 2H, ar.H), 6.82 (br s, 1H, -NH-), 6.41 (d, J = 15.8 Hz, 1H, CH=CH), 6.23 (dt, J = 15.8 Hz, 7.2 Hz, 1H, CH=CH), 3.86-3.82 (m, 2H, -CH₂OOC-), 3.60-3.56 (m, 2H, -C<u>H</u>₂NH-), 2.33-2.26 (m, 4H, -CH₂COO- und - C<u>H</u>₂CH=CH), 1.67-1.61 (m, 4H, alk.H), 1.55-1.52 (m, 2H, alk. H), 1.48-1.41 (m, 2H, alk.H), 1.39-1.35 (m, 2H, alk. H), 1.32-1.28 (br m, 10H, alk.H).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 174.4$ (-COO), 167.4 (-CONH), 141.1 (ar.C), 133.7 (ar.C), 129.7 (-CH=CH-), 127.4 (ar.C), 127.2 (ar. C), 125.7 (-CH=CH-), 65.00 (-<u>C</u>H₂OOC), 37.60 (-<u>C</u>H₂NHCO), 33.23 (-<u>C</u>H₂-COO), 31.97 (alk. C), 28.79 (alk. C), 28.51 (alk. C), 28.18 (alk.C), 27.32 (alk.C), 27.15 (alk. C), 26.91 (alk. C), 26.23 (alk.C), 25.55 (alk.C), 24.68 (alk.C), 21.91 (alk.C).

HRMS (FAB, 3-NBA) for $C_{24}H_{35}NO_3 [M]^+$: calcd.: 385.2617 found: 385.2619

6,7,8,9,10,11,15,16,17,18,19,20,21,22-Tetradecahydro-14*H*-13-oxa-6-azabenzocyclodocosen-5,12-dione (36)

The synthesis was performed according to **GP20** with 4.0 mg (0.0021 mmol Pd) Pd-beads **1a/Pd** or 2.4 mg (0.0021 mmol) Pd[PPh₃]₄, 13.7 mg (0.042 mmol) Cs_2CO_3 in 0.33 ml DME:H₂O:DMF (1.5:1.5:1) and 13.4 mg (0.021 mmol) 6-(2-iodobenzamido)-hexanoic acid 11-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-undec-10-enyl-ester (**94**) in 0.16 ml DME. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 1:1).

 $R_{f} = 0.35$ (cyclohexane:ethylacetate 1:1)

Yield: 4.6 mg (beads) (0.012 mmol, 58%) yellowish oil

4.7 mg (homogeneous) (0.012 mmol, 57%) yellowish oil

HPLC (C18): $t_R = 11.23 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): $\delta = 7.48$ (dd, J = 7.0 Hz, 1.4 Hz, 1H, ar. H), 7.44-7.42 (m, 1H, ar. H), 7.35 (dt, J = 7.6 Hz, 1.5 Hz, 1H, ar.H), 7.24 (dt, J = 7.4 Hz, 1.4 Hz, 1H, ar.H), 6.62 (d, J = 15.8 Hz, 1H, CH=CH), 6.18 (dt, J = 15.8 Hz, 6.6 Hz, 1H, CH=CH), 5.78 (br s, 1H, -NH-), 4.14 (t, J = 5.5 Hz, 2H, -CH₂OOC-), 3.44 (dt, J = 6.1 Hz, 7.5 Hz, 2H, -CH₂NH-), 2.34 (t, J = 7.5 Hz, 2H, -CH₂COO-), 2.23-2.17 (m, 2H, -CH₂CH=CH), 1.75-1.67 (m, 2H, alk. H), 1.66-1.55 (m, 4H, alk. H), 1.50-1.45 (m, 2H, alk. H), 1.42-1.36 (m, 2H, alk. H), 1.34-1.25 (m, 10H, alk. H).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.4$ (-COO), 169.4 (-CONH), 135.5 (ar.C), 135.1 (ar.C), 134.5 (ar.C), 130.0 (-CH=CH-), 127.8 (ar.C), 127.4 (ar.C), 127.0 (-CH=CH-), 126.5 (ar.C), 64.00 (-CH₂OOC), 39.85 (-CH₂NHCO), 34.81 (-alk. C), 32.77 (alk. C), 29.78 (alk. C), 28.94 (alk. C), 28.80 (alk. C), 28.63 (alk. C), 28.32 (alk. C), 28.18 (alk. C), 28.11 (alk. C), 26.91 (alk. C), 26.61 (alk. C), 25.30 (alk. C).

HRMS (FAB, 3-NBA) for $C_{24}H_{35}NO_3 [M]^+$:	cacld.:	385.2617
:	found:	385.2597
for C ₂₄ H ₃₆ NO ₃ [M+H] ⁺ :	calcd.:	386.2695
:	found:	386.2671

6,7,8,9,10,11,14,15,16,17-Decahydro-13-oxa-6-aza-benzocycloheptadecen-5,12-dione (35)

The synthesis was performed according to **GP20** with 4.0 mg (0.0021 mmol Pd) Pd-beads **1a/Pd** or 2.4 mg (0.0021 mmol) Pd[PPh₃]₄, 13.7 mg (0.042 mmol) Cs_2CO_3 in 0.33 ml DME:H₂O:DMF (1.5:1.5:1) and 11.4 mg (0.021 mmol) 6-(2-iodobenzamido)-hexanoic acid 6-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-hex-5-enyl-ester (**34**) in 0.16 ml DME. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 1:1).

 $R_f = 0.33$ (cyclohexane:ethylacetate 1:1)

Yield: 2.7 mg (beads) (0.00086 mmol, 41%) yellowish oil

3.8 mg (homogeneous) (0.013 mmol, 60%) yellowish oil

HPLC (C18): $t_R = 7.22 \text{ min}$

¹H-NMR (400 MHz, CDCl₃): $\delta = 7.50$ (dd, J = 7.5 Hz, 1.5 Hz, 1H, ar.H), 7.42-7.40 (m, 1H, ar.H), 7.35 (dt, J = 7.8 Hz, 1.5 Hz, 1H, ar.H), 7.25 (dt, J = 7.4 Hz, 1.4 Hz, 1H, ar.H), 6.68 (d, J = 16.0 Hz, 1H, CH=CH), 6.19 (dt, J = 15.8 Hz, 6.5 Hz, 1H, CH=CH), 5.75 (br s, 1H, -NH-), 4.21 (t, J = 6.2 Hz, 2H, -CH₂OOC-), 3.51-3.46 (m, 2H, -CH₂NH-), 2.39-2.36 (m 2H, -CH₂COO-), 2.28-2.22 (m, 2H, -CH₂CH=CH), 1.76-1.67 (m, 4H, alk. H), 1.64-1.52 (m, 4H, alk. H), 1.50-1.40 (m, 2H, alk. H).

¹³C-NMR (100 MHz, CDCl₃): $\delta = 173.7$ (-COO), 169.6 (-CONH), 135.6 (ar.C), 135.0 (ar.C), 133.9 (ar.C), 130.1 (-CH=CH-), 128.0 (ar.C), 127.9 (ar.C), 127.1 (-CH=CH-), 126.7 (ar.C), 63.27 (-CH₂OOC), 40.39 (-CH₂NHCO), 34.42 (alk. C), 31.94 (-alk. C), 29.35 (alk.C), 28.30 (alk. C), 27.03 (alk.C), 26.91 (alk.C), 24.98 (alk.C).

HRMS (FAB, 3-NBA) for $C_{19}H_{25}NO_3 [M]^+$:	calcd.:	315.1834
	found:	315.1867
for C ₁₉ H ₂₆ NO ₃ [M+H] ⁺ :	calcd.: found:	316.1913 316.1944

2,2-Dioxo-10-oxa-2λ6-thia-3-aza-bicyclo[15.2.2]heneicosa-1(20),15,17(21),18-tetraen-9one (36)

The synthesis was performed according to **GP20** with 4.0 mg (0.0021 mmol Pd) Pd-beads **1a/Pd** or 2.4 mg (0.0021 mmol) Pd[PPh₃]₄, 13.7 mg (0.042 mmol) Cs_2CO_3 in 0.33 ml DME:H₂O:DMF (1.5:1.5:1) and 11.4 mg (0.021 mmol) 6-(4-iodobenzenesulfonyl)-hexanoic acid 6-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-hex-5-enyl-ester (**97**) in 0.16 ml DME. The crude product was purified via flash chromatography (silica, cyclohexane:ethylacetate 1:1).

 $R_f = 0.35$ (cyclohexane:ethylacetate 1:1)

Yield: 2.1 mg (beads) (0.0063 mmol, 30%) yellowish oil

1.5 mg (homogeneous) (0.0046 mmol, 22%) yellowish oil

HPLC (C18): t_R = 7.88 min

¹H-NMR (400 MHz, CDCl₃): δ = 7.82 (d, *J* = 8.6 Hz, 2H, ar.H), 7.46 (d, *J* = 8.4 Hz, 2H, ar.H), 6.42 (d, *J* = 15.8 Hz, 1H, CH=CH), 6.31 (dt, *J* = 15.8 Hz, 7.2 Hz, 1H, CH=CH), 4.21 (t, *J* = 6.1 Hz, 1H, -NH-), 4.00 (t, *J* = 5.4 Hz, 2H, -CH₂OOC-), 3.09-3.05 (m, 2H, -C<u>H₂NH-), 2.28-2.23 (m, 2H, -CH₂COO-), 1.77-1.72 (m, 2H, alk. H), 1.70-1.67 (m, 4H, alk. H), 1.59-1.52 (m, 6H, alk. H).</u>

¹³C-NMR (100 MHz, CDCl₃): δ = 173.2 (-COO), 138.2 (ar.C), 128.9 (-CH=CH-), 127.8 (ar.C), 127.5 (-CH=CH-), 126.2 (ar.C), 63.69 (-<u>C</u>H₂OOC), 41.92 (-<u>C</u>H₂NHSO₂), 33.36 (alk.C), 32.24 (alk.C), 28.52 (alk.C), 26.92 (alk.C), 24.77 (alk.C), 24.55 (alk.C), 23.39 (alk.C).

LRMS (FAB, 3-NBA) for $C_{18}H_{25}NO_4S [M+H]^+$: calcd.: 352.16 found: 352.17

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